Cu$_2$O(100) surface as an active site for catalytic furfural hydrogenation


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

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**A B S T R A C T**

In order to investigate the major active site of Cu-based catalysts in furfural (FAL) hydrogenation, theoretical calculations were combined with empirical analyses. The adsorption of FAL and H$_2$ on the Cu(111), CuO(100), and Cu$_2$O(100) surfaces was compared based on density functional theory (DFT) calculations. The migration barrier of the dissociatively adsorbed H atoms on different surfaces was also calculated. It is demonstrated that the Cu$_2$O(100) surface has the largest FAL adsorption energy of 1.63 eV and an appropriate Cu‒Cu distance for adsorption and preferential dissociation of the H$_2$ molecule. To correlate the DFT results with catalytic experiments, mesoporous copper oxides (m-CuO) were prepared under controlled reduction conditions. The overall activity of the m-CuO catalysts is determined by the concentration of exposed Cu $^+$. The combined results from DFT calculations and experiments show that Cu$_2$O is a major active species promoting the high activity of FAL hydrogenation.

1. Introduction

Determining the active site on the surface of catalysts and describing the relevant reaction mechanism are crucial undertakings for the development of more efficient catalysts. Evaluating which phase critically affects the activity and selectivity of a reaction is of paramount importance, especially as the phase can change easily in catalytic reactions under various temperature and pressure conditions. Catalytic hydrogenation is essential for the conversion of cellulose and lignin, which contain a large amount of oxygen, into biofuels and high-value-added chemicals [1–3].

Biomass conversion has been extensively researched, where furfural (FAL) hydrogenation is a model reaction that is widely explored in the development of catalysts and understanding their reactivity and selectivity, due to the defined reaction pathways [4–10]. FAL hydrogenation proceeds via two major reaction pathways: furan (FR) or tetrahydrofuran (THF) formation by decarbonylation, or hydrogenation to furfuryl alcohol (FA), 2-methyl furan (MF), or tetrahydrofurfuryl alcohol (THFA). Many noble metal catalysts exhibit excellent reactivity in FAL hydrogenation, but they produce a variety of products, including the five major products mentioned above. Notably, examples of catalytic reactions in which the selectivity for one product is greater than 80% or the number of products is less than two are very rare. The formation of various byproducts is a major obstacle in the study of kinetics in catalysis. From this point of view, Cu-based catalysts are known to exhibit excellent FA selectivity in FAL hydrogenation and are useful for evaluating the mechanism of catalysis because the main products, other than FA and FR, are produced in extremely low concentrations [11–18].

One well-known catalyst for gas-phase FAL hydrogenation with high selectivity toward FA is copper chromite, where the active site includes Cu$^+$ and/or Cu$^+$ species. Rao et al. reported that the turnover frequency of the CuCrO$_2$ catalyst increased as the number of Cu$^+$ sites increased, but the Cu$^+$ site was also required [12]. They validated the Langmuir–Hinshelwood model, which includes a bimolecular surface reaction of FAL and H$_2$ as the rate-determining step over dual sites consisting of Cu$^+$ and Cu$^+$ [13]. Ghoshgheae et al. reported that Cu$^+$ of Cu/MgO catalysts was an active site for hydrogenation of FAL [19,20].

Density functional theory (DFT) calculations showed that the binding of Cu to MgO was stronger than that on SiO$_2$, resulting in different intermediates (an alkoxide intermediate instead of a hydroxylalkyl species). It was revealed that Cu catalyzed FAL hydrogenation was influenced by the type of support. Nagaraja and coworkers also reported that Cu$^+$ and Cu$^+$ were both necessary for the hydrogenation of FAL to FA over Cu/MgO catalysts [14,15]. Interestingly, they showed that when more Cu$^{2+}$ species were present in the Cu catalyst, the activity was lower. Nevertheless, in many studies of Cu-catalyzed reactions, there has been much debate about the identity of the active sites of the Cu catalysts. The relative proportions of Cu$^+$, Cu$^+$, and Cu$^{2+}$ depend on the preparation method of supported Cu catalysts and the pretreatment condition for reduction [21,22]. Thus, the assignment of the active sites is a critical area of study.

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phase of copper oxide differed depending on the catalytic reaction conditions, the surface structure of the catalyst, and adsorbate- or support-induced changes in the surface properties during the catalytic reaction using copper oxide having several oxide forms. Wang et al. reported that the Cu$_2$O phase was not readily detectable under hydrogen reduction conditions, while it suffered sequential reduction (CuO $\rightarrow$ Cu$_2$O $\rightarrow$ Cu) involving the Cu$_2$O intermediate under a limited supply of CO [21]. They also demonstrated that the Cu$_2$O-like intermediate has an extra disordered oxygen at the empty tetrahedral sites, which might play an important role in adsorbing the reactants.

Nanocasting as a hard-template approach has been widely used for the preparation of various mesoporous materials including CuO. When internal pores of the mesoporous silica with a well-ordered pore structure are filled with metal salts in solution, oxide replicas are produced by heat treatment and subsequent removal of the template by NaOH solution [23]. When mesoporous silica, KIT-6 with interconnected cubic pore structures is used in the presence of copper nitrate, the CuO replica with cubic pore structures (Ia3d) is produced. Through controlled reduction by H$_2$, mesoporous CuO (m-CuO) is converted to Cu$_2$O and finally Cu. Many supported Cu catalysts have been investigated to find surface active sites. However, highly dispersed Cu species on the support is difficult to characterize due to its very small portion compared to the support. Crystalline m-CuO with high surface area and well-defined pore structure is suitable for generating distinct surface species of Cu$^{2+}$, Cu$^+$, and Cu$^0$ phases on the surface [10].

Herein, DFT calculations are used to investigate the active sites of Cu-based catalysts for FAL hydrogenation. The adsorption of FAL and H$_2$ on the Cu(111), CuO(100), and Cu$_2$O(100) surfaces are compared. The migration barrier of the dissociatively adsorbed H atom on different surfaces is also calculated. Completion of FAL hydrogenation to produce FA by transfer of H atoms to the FAL intermediate was also studied. To correlate the DFT results with the catalytic experiments, a series of m-CuO catalysts is prepared under controlled reduction conditions and the activity and selectivity for FAL hydrogenation are compared. The effect of the reduction temperature on the crystal structure, porosity, and oxidation state of catalysts is characterized to determine which Cu active species critically influence the catalytic performance for FAL hydrogenation. The distribution of Cu species (Cu$^{2+}$, Cu$^+$, and Cu$^0$) in the catalysts is correlated with the catalytic activity for FAL hydrogenation, revealing that the higher the distribution of Cu$^+$, the higher the activity for FAL hydrogenation. The calculated migration barrier of the dissociated H atoms on the CuO(100) surface agrees well with the H$_2$ binding energy obtained from the temperature-programmed H$_2$ desorption data.

2. Experimental

2.1. DFT calculation

All calculations were carried out in the framework of the spin-polarized DFT using the Vienna ab initio simulation package (VASP) with the projector-augmented wave (PAW) method [24–26]. The generalized gradient approximation of Perdew–Burke–Ernzerhof (PBE) was used to consider the exchange-correlation [27]. The cut-off energy for the plane wave basis set was 500 eV and the ionic positions of all structures were relaxed until the force converged to below 0.01 eV Å$^{-1}$. A k-point mesh of 1-centered 2 × 2 × 2 set was adopted. To study the adsorption of FAL and H$_2$ on the catalysts, (4 × 4), (2 × 2), and (2 × 2) super-cells were used for the Cu(111), CuO(100), and Cu$_2$O(100) surfaces with four Cu layers. For the hydrogenation process on Cu$_2$O (100) surface, $\sqrt{2} \times \sqrt{2}$ unit-cell was used, because the plane of the attached FAL molecule is parallel to the diagonal direction. The unit cell shows the minimum value of the hydrogenation process by reducing the interaction between unit cells (Fig. S1). The vacuum between slabs along the z-direction was set at a minimum of 12 Å to minimize interactions between the slabs and reduce the complexity of the calculation. The two bottom Cu layers of all the slab systems were fixed to the corresponding bulk-optimized position. Because Cu metal systems with a large U (electron-electron correlation parameter) caused suspicious band gap, we did not adopt U values for all systems for consistent comparison of properties [28]. In all calculations, spin polarization was considered for surface magnetism to set CuO as a type-II antiferromagnetic [29]. The nudged elastic band (NEB) method was used to calculate the migration barriers of hydrogen in the expected diffusion pathways on the Cu$_2$O(100) surface [30]. The van der Waals interaction was not considered, because the estimated energy scale of the interaction is less than 0.1 eV [31,32]. The van der Waals interaction can be important if the FAL’s aromatic ring plane is parallel to the surface at a distance of ~ 3 Å [33,34], but is not observed in the current calculations. The terminal oxygen atom of FAL is adsorbed on the surface oxygen vacancies of Cu$_2$O(100) surface, indicating a chemical bond between FAL and Cu$_2$O(100) surface, which is stronger than the van der Waals interaction.

2.2. Catalyst preparation

Copper oxides with a well-ordered porous structure were synthesized by the nanocasting method [23]. Mesoporous silica, KIT-6, with a cubic Ia3d mesophase was used as a template. KIT-6 silica was prepared via a well-known cooperative assembly process, in which the Ia3d mesophase was formed by the triblock copolymer in acidic solution [35,36]. In order to prepare KIT-6, 27 g of Pluronic P123 (PEO$_{20}$–PPO$_{70}$–PEO$_{20}$) (Sigma-Aldrich) was dissolved in 980 mL of water and 43.5 mL of concentrated HCl at 35 °C. Thereafter, 33.3 mL of butanol was added to the solution with vigorous stirring and the resulting mixture was stirred continuously for 6 h at 35 °C. After adding 62.2 mL of tetraethyl orthosilicate (Sigma-Aldrich), the mixture was maintained at the same temperature for another 24 h. The hydrothermal process was then performed at 80 °C under static conditions. The resulting solution was filtered, dried overnight at 90 °C, and calcined in air at 550 °C for 6 h to obtain the mesoporous silica, KIT-6.

M-CuO was prepared via nanocasting by using the KIT-6 template [37]. Briefly, 24 mmol of copper nitrate (Cu(NO$_3$)$_2$·2.5H$_2$O; Sigma-Aldrich) was dissolved in 6 mL of deionized water. The solution was added to 6 g of KIT-6 in 50 mL of toluene at 65 °C under stirring. After evaporation of the toluene, the precipitate was collected and dried at 60 °C overnight, followed by calcination at 300 °C for 5 h. The silica template was completely removed using 2 M aqueous NaOH solution heated to 90 °C. The resulting solid was collected by centrifugation and washed with water. After 4 cycles of silica etching with the NaOH solution and subsequent washing with water, the resulting powder was collected and dried at 50 °C; this sample is hereinafter termed m-CuO. To change the crystal structure and surface oxidation state, as-prepared m-CuO was further reduced under H$_2$ (4% H$_2$ in Ar, flow rate = 100 mL·min$^{-1}$) at 150, 250, and 350 °C for 1 h. The reduced products are respectively denoted as m-CuO-150, m-Cu-250, and m-Cu-350, indicative of their major bulk crystal structure and reduction temperature.

2.3. Catalyst characterization

Powder X-ray diffraction (XRD) patterns were recorded on a PANalytical X'Pert PRO diffractometer using Cu-Kα radiation ($\lambda$ = 0.154056 nm). In situ XRD study under reducing conditions was performed on a SmartLab (Rigaku) X-ray diffractometer equipped with a D/teX Ultra 250 detector using Cu-Kα radiation ($\lambda$ = 1.54184 Å) at a scanning rate of 3°·min$^{-1}$ in the 2θ range of 10–80° [37]. The catalyst was placed in a Kanthal (FeCrAl) filament cavity, and the temperature was increased from 50 to 600 °C under a flow of 4.0 vol.% H$_2$ in Ar at a flow rate of 150 mL·min$^{-1}$. X-ray photoelectron spectroscopy (XPS)
analysis was carried out on a K-alpha (ThermoFisher) system equipped with an Al-Kα X-ray (hv = 1486.6 eV) excitation source. The specific surface area of the catalysts was determined from the N2 adsorption/desorption isotherms collected on a BELSORP-max unit. The pore size and distribution of the catalysts were calculated by the Barrett–Joyner–Halenda (BJH) method. X-ray absorption spectroscopy (XAS) analysis was also carried out at Beamline 6D of the Pohang Accelerator Laboratory (PAL) using an electron beam energy of 3.0 GeV; the current of the incident X-ray was 300 mA [10]. A Si(111) double-crystal monochromator was used to filter the incident photons. X-ray absorption near-edge structure (XANES) spectra in the Cu K-edge region were collected in transmission detection mode. XAS data were interpreted by ATHENA software [38], and the spectra were aligned based on the first oscillation in EXAFS region. XANES spectra of each catalyst were compared after normalizing based on pre-edge and atomic background removal. Transmission electron microscopy (TEM; JEOL JEM-1400) was used for structural characterization, at an acceleration voltage of 200 kV. High-resolution TEM (HR-TEM) images were also acquired on a JEOL JEM-2100 F electron microscope. The temperature-programmed reduction by H2 (H2–TPR) was evaluated using an Auto Chemil 2920 instrument (Micromeritics Instruments Co., USA). Prior to reduction, m-CuO was pretreated under a He flow of 30 mL·min−1 at 100 °C for 30 min to remove the residual oxygen. For the TPR run, m-CuO was placed in a quartz reactor and heated to 800 °C at a constant heating rate of 10 °C·min−1 under 10 % H2/He flow at a rate of 30 mL·min−1. Temperature-programmed desorption of hydrogen (H2–TPD) was conducted in BELCAT II (Micromeritics Instruments Co., Japan). Prior to the desorption experiment, the surface of m-CuO was saturated with hydrogen at 150 °C for 2 h with 50 mL·min−1 of pure H2. The reduced m-CuO was heated from −100 °C to 700 °C, and each trial had different ramping rate (2, 5, 10, and 15 °C·min−1) under pure He flow. The apparent energy for hydrogen migration was evaluated with the H2–TPD experiment using the Kissinger equation,

\[
\frac{d(\ln \frac{\beta}{\beta_{\text{max}}})}{d(\frac{1}{T_{\text{max}}})} = - \frac{E_a}{R}
\]

where \(\beta\) is the heating rate, \(T_{\text{max}}\) is the maximum temperature of the peak, \(R\) is the gas constant and \(E_a\) is the activation energy for migration of hydrogen [39,40]. Diffuse reflectance infrared spectra (DRIFTS) were acquired with a Nicolet is10 FTIR spectrometer equipped with a mercury-cadmium-telluride (MCT) detector. Each catalyst (15 mg) was loaded into the reaction chamber (Harrick Scientific) with ZnSe window samples and a Praying Mantis diffusion reflection accessory. After He purging to remove ambient air, the sample was cooled to −153 °C under He flow (1 mL·s−1) and the background spectrum was collected. CO adsorption was carried out with 0.2 % CO/He at a flow rate of 1 mL·s−1 for 10 min; the sample was purged with He to remove weakly bound CO. All spectra were obtained with an average of 128 scans at a resolution of 4 cm−1.

2.4. Reaction procedure and product analysis

A stainless-steel high-pressure reactor with an inner volume of 100 mL was used for liquid-phase FAL hydrogenation [9,10]. FAL (1 g, Acros, 99 %) was mixed in 20 mL of isopropanol (Sigma-Aldrich, 99.5 % anhydrous) in the presence of the catalyst and poured into the reactor. After flushing with hydrogen, the reactor was pressurized to 2 MPa with hydrogen, then heated to 180 °C and maintained at 600 rpm with stirring for 5 h. After completion of the reaction, the resulting liquid product was collected and filtered through a 0.2 μm membrane filter to ensure a particle-free solution before further analysis. The liquid product was analyzed by gas chromatography (GC) using a flame ionization detector (FID, Agilent 7820A) equipped with a capillary column (DB-WAX, length: 30 m, internal diameter: 0.32 mm, and film thickness: 0.25 μm). The following temperature program was repeated: hold at 50 °C for 3 min, increase the temperature to 50–100 °C at a rate of 10 °C·min−1, hold for 3 min, increase the temperature to 100–200 °C at a rate of 25 °C·min−1, and hold for another 3 min. The DB-WAX column was calibrated by using commercial chemicals including FA (Sigma-Aldrich, 98 %), FR (Sigma-Aldrich, 99 %), THF (Alfa Aesar, 99 %), and MF (Sigma-Aldrich, 99 %). The conversion was calculated by the number of consumed FAL molecules, and the product selectivity was determined by the relative proportions of products produced as follows:

\[
\text{Conversion(\%)} = \frac{\text{mol FAL consumed}}{\text{mol FAL fed}} \times 100
\]

\[
\text{Selectivity(\%)} = \frac{\text{mol product formed}}{\sum \text{mol products formed}} \times 100
\]

The reaction rate was calculated in two ways. Surface activity was calculated by the surface area of catalyst, and mass activity was normalized by the total grams of catalyst. In addition, the reaction rate was further calculated by conversion per Cu+ fraction of the total grams of catalyst.

3. Results and discussion

3.1. DFT calculation for Cu(111), CuO(100), and Cu2O(100) surfaces

The mechanism of catalytic hydrogenation of FAL is thought to occur via three steps: (1) adsorption of FAL, (2) adsorption and dissociation of H2, migration of the dissociated H atoms, and (3) completion of hydrogenation of FAL. Herein, DFT study was carried out to calculate the adsorption energy of FAL, the dissociation energy of H2, and the barrier for migration of H and completion of FAL hydrogenation to FA (Scheme 1).

In step 1, the energy for the adsorption of FAL on selected Cu-based surfaces was calculated, indicating the reaction probability. In step 2, the energy for adsorption of the H2 molecules on the catalyst surface was evaluated. The adsorbed H2 molecules were dissociated and migrated along the surface by overcoming the dissociation barrier and the migration barrier, respectively. In step 3, hydrogenation is completed whereby the migrating H atom approaches FAL by overcoming the reaction barrier. Because Cu metal has a filled d-orbital, a repulsive force develops between the d-orbital of Cu and p-orbital of the furan ring of FAL. FAL adsorption on the Cu metal preferentially occurs in an “upright” configuration perpendicular to the Cu surface without adsorption of the furan ring [8,16]. Thus, we considered FAL adsorption only through the terminal oxygen atom on all Cu, CuO, and Cu2O species. For the DFT calculation, Cu(111), CuO(100), and Cu2O(100) were selected as the model surfaces. The CuO(100) surface is known to have half of the surface oxygen and half of the vacancy site with a c(2 × 2) surface structure [34], where FAL molecules can be adsorbed to the oxygen vacancies. On the CuO(111) and Cu2O(111) surface, all oxygen sites will be occupied under the stoichiometric condition [26] but such FAL adsorption is rare. The CuO(100) surface, where half of the oxygen site is unoccupied, can be the adsorption site of FAL. However, the Cu2O(111) surface with zero net surface normal dipole has no reconstruction or redistribution of terminal atoms to adsorb FAL. The adsorption energy of FAL was determined as follows: \(E_{\text{ads}} = E_{\text{surface + FAL}} - E_{\text{surface}} - E_{\text{FAL}}\). Fig. 1 shows the top view of the respective Cu(111), CuO(100), and Cu2O(100) surfaces. For comprehensive evaluation of the surface structure, the outermost layers of Cu(111), CuO(100), and Cu2O(100) surfaces. For comprehensive evaluation of the surface structure, the outermost layers of Cu(111), CuO(100), and Cu2O(100) surfaces. For comprehensive evaluation of the surface structure, the outermost layers of Cu(111), CuO(100), and Cu2O(100) consisting of the outermost Cu layer and two outer O layers are shown. The oxygen atoms in the outermost layer are distinguished by having a larger radius than the other oxygen atoms. The Cu atoms of the Cu(111) surface, selected as the most stable of the Cu surfaces, are separated by a constant Cu–Cu distance of 2.568 Å (Fig. 2a). The calculated energy for the adsorption of FAL on the Cu (111) surface was as small as −0.168 eV (Fig. 1a) due to the weak
interaction between these species. The relatively stable CuO(100) and Cu_2O(100) surfaces have adsorption energies of -0.719 eV and -1.630 eV for FAL, respectively (Fig. 1b, c). Tasker et al. reported that the type 3 surface with surface normal dipoles had oxygen vacancies (O_{vac}) that reduced the energy cost from the surface normal dipoles, with anion redistribution on the opposite surface under stoichiometric conditions [36]. It is consistent with the experimentally observed c(2 × 2) Cu_2O(100) surface structure [34]. The reconstructed CuO(100) surface was compared with the other distribution, as shown in Fig. S2. The reconstructed structure of the CuO(100) surface has a surface oxygen at the center of a triangular array of Cu atoms, forming three Cu–O bonds; the shortest Cu–Cu distance among the oxygen-deficient Cu triangles is 2.919 Å (Fig. 2b). In the Cu_2O(100) surface structure, the oxygen atoms of the two outer layers connect the outermost Cu atoms obliquely and the structure is most stable with two O_{vac} on the same diagonal; the shortest Cu–Cu distance with an O_{vac} is 2.429 Å (Fig. 2c, Table S1). The O_{vac} sites on the CuO(100) and Cu_2O(100) surfaces provide a good position for the adsorption of FAL via the oxygen of the aldehyde group. The highest adsorption energy of FAL on the Cu_2O(100) surface indicates that FAL is preferentially attached to this surface with the highest possibility for reaction, as shown in Step 1 (Scheme 1).

H_2 adsorption and dissociation on the surfaces was also investigated. In the optimal surface structures, the shortest Cu–Cu distance of the Cu(111), CuO(100), and Cu_2O(100) surfaces was 2.568, 2.919, and 2.429 Å, respectively (Fig. 2a–c). The Cu–Cu distance of the CuO(100) surface is too long for the adsorption of H_2. However, the Cu_2O(100) surface has the shortest Cu–Cu distance and is thus amenable to the preferential adsorption and dissociation of H_2. The Cu–Cu distance of the Cu(111) surface is similar to that of Cu_2O(100); however, as discussed above, this surface was not given further consideration due to its weak interaction with FAL. Although the Cu(111) surface may contribute to supplying H to FAL, the effect is very small for FAL hydrogenation based on our calculations. To compare the Cu(900) and Cu_2O(100) surfaces, the H_2 adsorption and dissociation behavior was predicted to determine the low energy is determined in the unit-cell with a preferential axis (Fig. S1). As a result of performing NEB calculations (Fig. S3), the Cu_2O(100) surface is easily dissociated (E_{ads} = -3.337 eV). Because geometric optimization in the calculation assumes a temperature condition of zero, the dissociation of H_2 molecules occurs without a finite temperature and barrier.

As step 2, the energy for the migration of dissociated H atoms along the surface of Cu_2O(100) by overcoming the dissociation and migration barrier was also calculated. However, DFT results are discussed along with the experimental data in the next section. The step 3 process of FAL hydrogenation on Cu_2O(100) surface was investigated by DFT calculations. As FAL is adsorbed to O_{vac} site of the Cu_2O(100) surface along the surface Cu–O chain direction, the optimal configuration of low energy is determined in the unit-cell with a preferential axis (Fig. S2). It is assumed that the H atom approaches the FAL molecule attached through the H migration path, which will be discussed later and is located between the Cu chains forming Cu–H–Cu bonds near the FAL as indicated by the red dot (Fig. S1). As a result of performing NEB calculation through hydrogenation of the C atom of the carbonyl group in FAL, the resulting reaction barrier of the C atom was 1.01 eV, and the H migration to O atom was 0.82 eV (Fig. S3). Because the barrier is somewhat higher than expected, other hydrogenation pathways with lower barriers are considered. The high hydrogenation barrier is due to the long distance between the C atom and the H site (2.78 Å). To reduce the distance, a new configuration was created by tilting the FAL molecule towards the H site. The calculated energy with the tilted structure of FAL on the CuO(100) surface was 0.5 eV higher than the straight structure (Fig. S3). The hydrogenation process based on the tilted FAL structure of the CuO(100) surface were calculated through NEB calculations (Fig. 3 and Fig. S4). Three hydrogenation processes...
with a tilted FAL configuration including hydrogenation to C atom of carbonyl group in FAL, hydrogenation to O atom of carbonyl group in FAL, and hydrogenation to O atom with additional H atoms after the first hydrogenation to C atom are shown in Fig. 3. In addition to the front view (Fig. 3), side views of the initial (init), transition (trans), and final state structures are also provided in Fig. S4. The calculated barrier for hydrogenation to C atom of a carbonyl group with the tilted FAL configuration was 0.55 eV, which is lower than the value obtained from the straight structure (Fig. 3a). The final hydrogenated structure to C atom has an energy of 1.28 eV, which is lower than the original structure before hydrogenation. The energy calculated from the hydrogenated structure to O atom is 0.53 eV, which is higher than the structure before the hydrogenation. The reaction barrier is 0.86 eV (Fig. 3b). It indicates that the hydrogenation process begins with the hydrogenation of C atom, followed by the hydrogenation of O atom with additional H atoms, because the first step towards C atom is energetically favorable. The hydrogenation of O atom with additional H atom is shown in Fig. 3c. The second hydrogenation process is exothermic with an energy of 0.65 eV lower than the initial, and the reaction barrier is only 0.12 eV. In the DFT calculation results, the highest barrier during the hydrogenation process is 0.55 eV of the first hydrogenation to C atom of FAL, and the next barrier during the second hydrogenation to O of FAL is 0.12 eV, and the entire process is exothermic. The highest barrier of 0.55 eV during hydrogenation will be discussed in the next section with the H migration barrier compared to the experimental results.

3.2. Preparation and characterization of Cu-based catalysts

In order to correlate the DFT results with catalytic experiments, we
prepared mesoporous copper oxides under controlled reduction conditions and carried out catalytic FAL hydrogenation. Copper oxides with mesoporous structures were prepared by the nanocasting method using mesoporous silica, KIT-6 (Fig. 4a) [35,36]. Because of the well-ordered mesostructure of the KIT-6 template, the resulting mesoporous copper oxide had a double-gyroid pore structure with cubic $Ia3d$ symmetry [23]. When the mesoporous copper oxide ($m$-CuO) was reduced by hydrogen at different temperatures, the overall crystalline phase of copper oxide changed gradually. The morphological change of the $m$-CuO series was characterized by TEM (Fig. 4b). Highly ordered mesoporous CuO with a pore symmetry of $Ia3d$ is apparent in Fig. 4b. TEM image of $m$-CuO-150 shows that the original ordered mesoporous structures were maintained after reduction at 150 °C. However, the ordered mesoporous structure collapsed substantially after reduction at 250 and 350 °C. The $m$-CuO series presented typical type-IV in nitrogen adsorption-desorption isotherms [41], indicating that the ordered mesoporous structure was retained in all catalysts, except for metallic Cu, after reduction at 250 and 350 °C (Fig. S5). The specific surface area, mean pore diameter, and pore volume of the $m$-CuO series are presented in Table S2. The specific surface area of $m$-CuO decreased from the initial value of 46 m$^2$‧g$^{-1}$ as the reduction temperature increased from 150 to 350 °C. This is attributed to partial or complete destruction of the mesostructure during the phase transformation from CuO to metallic Cu under H$_2$ reduction conditions.

To characterize the Cu$_2$O(100) crystal phase of $m$-CuO-150, HR-TEM images were analyzed with selected area fast Fourier-transform (FFT) patterns (Fig. 4c and Fig. S6). As shown in Fig. 4c, the selected area electron diffraction patterns of $m$-CuO-150 show that as-prepared $m$-CuO has nano-sized crystalline Cu domains. The FFT patterns show that Cu$_2$O(111) and/or Cu$_2$O(100) are present with CuO species by incomplete reduction of $m$-CuO-150 at 150 °C. Although the amount of Cu$_2$O(100) fraction in the $m$-CuO-150 catalyst was not clearly characterized, the presence of the Cu$^+$ (100) phase was confirmed. HR-TEM images of $m$-CuO-150 catalysts with corresponding FFT patterns as shown in Fig. 4c, CuO and Cu$_2$O phases are mixed. By analyzing the displacing value of HR-TEM images and the lattice distance obtained from FFT spots, Cu$_2$O(111) and Cu$_2$O(100) phases are mixed. By analyzing the displacing value of HR-TEM images and the lattice distance obtained from FFT spots, Cu$_2$O(111) and Cu$_2$O(100) phases are mixed. By analyzing the displacing value of HR-TEM images and the lattice distance obtained from FFT spots, Cu$_2$O(111) and Cu$_2$O(100) phases are mixed. By analyzing the displacing value of HR-TEM images and the lattice distance obtained from FFT spots, Cu$_2$O(111) and Cu$_2$O(100) phases are mixed. By analyzing the displacing value of HR-TEM images and the lattice distance obtained from FFT spots, Cu$_2$O(111) and Cu$_2$O(100) phases are mixed.
prepared m-CuO comprises phase-pure CuO. The original CuO phase was maintained in m-CuO that was reduced under hydrogen at 150 °C (m-CuO-150); however, the peak intensity decreased substantially and a very small peak appeared at 36.4°, corresponding to the reflection from the (111) plane of Cu2O. The Cu2O intermediate phase was also identified in m-Cu-250 reduced under hydrogen at 250 °C, although the major crystal structure was fcc Cu. After reduction at 350 °C, the oxide was fully reduced to fcc Cu. The in situ XRD data presented in Fig. 5b demonstrate a sequential reduction pathway (CuO → Cu2O → Cu) of m-CuO under reducing environment at different temperatures [21]. The CuO phase was observed until the reduction temperature reached 250 °C and disappeared thereafter, with the appearance of the metallic Cu peak after 300 °C. This indicates that the CuO phase was completely reduced to metallic Cu above 300 °C and phase transformation was dramatic at temperatures of 150–250 °C. It is consistent with the H2-TPR profile of m-CuO catalyst (Fig. S7). Along with the phase transformation from CuO to metallic Cu, m-CuO was not fully reduced by H2 at 150 °C, where CuO and Cu2O phases were still present. Likewise, Cu2O and metallic Cu were co-existent in m-Cu-250.

The surface composition and oxidation state of the m-CuO series were investigated by XPS Cu 2p and Auger Cu LMM spectra (Fig. 5c). The Cu 2p spectra of the m-CuO series reduced at different temperatures exhibit two oxidation states. The peak (Cu 2p3/2) at 933.3 eV is attributed to Cu2+. Satellite peaks at 940.9 and 943.2 eV provide evidence of CuO [17]. As the reduction temperature increased, the CuO satellites disappeared and the portion of the Cu2+ peak at 933.3 eV decreased. The peak at the binding energy of 932.4 eV is attributed to two species: Cu+ and Cu°. It is difficult to separate, because the binding energies of Cu+ and Cu° are located too close (Cu+ at 932.18 eV and Cu° at 932.63 eV) [42]. However, the degree of reduction could be observed by comparing the intensity and binding energy between peaks of the m-CuO series. The higher peak intensity at 932.4 eV, the (Cu+ + Cu°)/Cu2+ ratio increases with increasing reduction temperature (0.2, 1.6, 5.0, and 10.1 for m-CuO, m-CuO-150, m-Cu-250, and m-Cu-350, respectively) (Table S4). Another information is provided by the highest peak position to determine the dominant state between Cu+ and Cu° obtained. In the Cu 2p3/2 spectrum of m-CuO, the binding energy of the Cu°/Cu+ peak is close to that of the Cu+ species (933.18 eV). As the reduction temperature increases further, the peak shifts much closer to the binding energy of the Cu° (932.63 eV). The Cu 2p3/2 spectrum of m-Cu-350 shows a sharp peak without the shake-up satellite of the CuO species, showing that the surface of m-CuO dominantly reduced to Cu° at 350°C. The Auger Cu LMM profiles of the m-CuO series clearly show the reduction trend of m-CuO. The binding energy of Cu2+ is located at 569 eV, and the Cu+ and Cu° species are at 570 eV and 568 eV, respectively. The Cu LMM profile follows the same reduction trend of the m-CuO series shown in the Cu 2p3/2 spectrum. The peak of Cu2+ at 569 eV decreases with increased reduction temperature, while the peaks of Cu° and Cu+ increase markedly. XAS experiments were also conducted to reveal the detailed atomic structure of the m-CuO series (Fig. S8a). The characteristic CuO peak was clearly distinguished from those of CuO and Cu in the Cu K-edge XANES spectra, and the pattern of m-CuO-150 was similar to that of m-CuO with the CuO phase being dominant. Likewise, the spectrum of m-Cu-250 was similar to that of m-Cu-350 with metallic Cu. Unfortunately, the Cu2O phase was not apparent for all samples in the XANES spectrum.

Fig. 3. NEB calculation results of the hydrogenation process with tilted FAL configurations (front view) on the Cu2O(100) surface and reaction energy profiles depending on the migration stage (initial, transition, and final): (a) hydrogenation to C atom of carbonyl group in FAL, (b) hydrogenation to O atom of carbonyl group in FAL, and (c) the second hydrogenation to O atom with additional H atoms after the first hydrogenation to C atom.
DRIFT spectroscopy can clearly identify exposed copper sites after adsorption of the CO probe molecule [43–48]. CO-DRIFTS is known as one of the most useful methods for determining various Cu species, since various types of adsorbed CO on copper-based surface appear in the carbonyl stretching region (2000–2200 cm⁻¹) [46,44–48]. In particular, the main band of 2120–2136 cm⁻¹ is clearly assigned to the CO adsorbed Cu⁺ species, because the Cu⁺−CO species is very stable due to the σ- and π-back bonds with CO. Because there is no overlap between peaks, the CO-DRIFTS is very sensitive and reliable in identifying and quantifying the relative fractions of CuO, Cu₂O, and Cu in the m-CuO catalysts. Fig. 5d shows the DRIFT spectra of the m-CuO series with adsorbed CO, prepared at different reduction temperatures. The band at 1800–2300 cm⁻¹ indicates adsorbed CO on the metal surface and the strong band at 2158 cm⁻¹ is attributed to CO adsorbed on the exposed Cu²⁺ sites [43–45]. The band at ca. 2125 cm⁻¹ is assigned to adsorption at the Cu⁺ site, whereas the Cu⁺ site is indicated by the band at 2102–2118 cm⁻¹ [44]. The spectrum of m-CuO shows a broad band around 2158 cm⁻¹ with a shoulder at 2125 cm⁻¹, indicating that the main exposed copper site on the catalyst surface is Cu²⁺. Reduction at 150 °C intensified the 2125 cm⁻¹ peak while reducing the intensity of the 2158 cm⁻¹ peak, indicating that m-CuO-150 comprised a mixture of Cu²⁺ and Cu⁺ species. Increasing the reduction temperature to 250 °C further reduced the intensity of the 2158 cm⁻¹ peak and revealed the appearance of a broad peak at 2104 cm⁻¹. This observation indicates that a small portion of the Cu²⁺ form was retained, and the Cu surface then comprised a mixture of Cu⁺ and metallic Cu°. After reduction at 350 °C, the strong peak of m-Cu-350 at 2104 cm⁻¹ provides evidence that the Cu⁺ species was substantially converted to the metallic Cu, although it still shows the Cu²⁺ band at 2158 cm⁻¹. The presence of Cu²⁺ on the surface of m-Cu-350 is due to the re-oxidation of the Cu surface exposed to air while handling the samples for characterization or catalytic reaction. In order to eliminate the possibility of surface re-oxidation of the Cu surface by air, additional DRIFTS experiments of m-Cu-350 were performed in air-tight condition. When the DRIFT spectrum of m-Cu-350 was obtained by in situ reduction at 350°C in the cell, a separated band of Cu° sites at 2112 cm⁻¹ appeared without the CO adsorbed Cu²⁺ bands. From these results, m-CuO was demonstrated to be reduced to Cu via a sequential pathway involving the Cu₂O intermediate. The m-CuO series contains different proportions of the cupric (Cu²⁺), cuprous (Cu⁺), or metallic (Cu°) phase, depending on the
reduction temperature. In most cases, the surface Cu is in one or more oxidation states. In order to quantify the fraction of Cu in each valence state, each fraction was assumed to be proportional to the area under the deconvoluted peak corresponding to the respective oxidation states. The corresponding fractions of each Cu oxidation state obtained from deconvolution of the DRIFT spectra (Fig. S8b) are listed in Table S2 for all catalysts. It is confirmed that Cu$^{2+}$ comprised 90.7 % of the exposed Cu surface sites in m-CuO, while the proportion of Cu$^{+}$ was 9.3 %. After reduction at 150 °C, the ratio of Cu$^{2+}$ decreased to 57.2 %, while the Cu$^{+}$ fraction increased to 42.8 % in m-CuO-150. After reduction at 250 °C, the Cu$^{2+}$ fraction rapidly decreased to 11.8 %, with the appearance of 47.2 % of metallic Cu (m-Cu-250). Reduction at 350 °C resulted in an increase in the metallic Cu fraction (67.0 %), with a remarkable decrease in the Cu$^{+}$ fraction (11.4 %) (m-Cu-350). The fraction of Cu$^{2+}$ on the surface of m-Cu-350 increased to 21.6 % due to re-oxidation of the Cu surface in air. The m-Cu-350 catalyst obtained by in situ reduction at 350 °C in the cell shows no Cu$^{2+}$ component, but there are Cu$^{+}$ (9.0 %) and Cu$^{0}$ (91.0 %) species on the surface.

Fig. 5. (a) XRD, (b) in situ XRD, (c) XPS Cu 2p$_{3/2}$ spectra and Auger Cu LMM Auger peaks for m-CuO series prepared at different reduction temperatures, and (d) DRIFT spectra after CO adsorption on various m-CuO series. *The asterisk indicates m-Cu-350 catalyst reduced by the in situ H$_2$ environment in the DRIFT cell.

Table 1
Results of catalytic FAL hydrogenation over m-CuO catalysts.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Reduction temp. (°C)</th>
<th>Reaction temp. (°C)</th>
<th>Conversion (%)</th>
<th>Surface activity [mol h$^{-1}$ m$^{-2}$] ($\times 10^3$)</th>
<th>Mass activity [mol h$^{-1}$ g$^{-1}$]</th>
<th>Selectivity (%)</th>
<th>FA</th>
<th>FR</th>
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<td>180</td>
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<td>7.18</td>
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<td>75</td>
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<tr>
<td>3$^b$</td>
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</table>

* Reaction conditions: FAL: 1 g, isopropanol: 20 mL, catalyst: 10 mg, H$_2$: 2 MPa, reaction time: 5 h.
$^b$ Reaction time: 3 h.
Fig. 6. Results of catalytic FAL hydrogenation: (a) illustration of reaction pathways and corresponding major products. (b) Surface activity and reaction rate for FAL hydrogenation over m-CuO series at the reaction temperature of 180 °C. (c) Changes in FAL conversion and selectivity over m-CuO-150 as a function of reaction temperature.

3.3. Relationship between copper site and catalytic activity for FAL hydrogenation

The liquid-phase FAL hydrogenation reaction was carried out over the m-CuO series to investigate the relationship between the catalytic activity and the copper active sites. For the catalytic reaction, 1 g of FAL was dissolved in 20 mL of isopropanol in the presence of 10 mg of catalyst, and pressurized with hydrogen gas (2 MPa). The catalysis conversion, product yield, and reaction rate are summarized in Table 1. Under the current m-Cu catalyzed reaction conditions, the major products were only FA and FR with less than 5% of by-products (Fig. 6a). Isopropanol is known to be an excellent hydrogen donor solvent that promotes the transfer hydrogenation of FAL without external hydrogen [49,50]. However, when H2 was not used for the present FAL hydrogenation, 5% conversion was achieved with m-CuO-150, because no support with acid sites was used (Table S3). As shown in Table 1, 37% conversion of FAL was achieved over the as-prepared m-CuO with a mass activity of 0.076 mol h⁻¹ g⁻¹. Reduction of m-CuO under a flow of H2 at 150 and 250 °C caused the activity of the resulting catalysts (m-CuO-150 and m-Cu-250) to increase. In particular, much higher conversion was achieved with m-CuO-150 (99%) and m-Cu-250 (80%) than with the original m-CuO (37%), despite the smaller surface area of the former after the reduction. Surface activity calculated by the surface area of catalyst and mass activity normalized by the total grams of catalyst are used for comparison. For accuracy, the conversion of m-CuO-150 was measured after the 3 h of reaction to achieve the conversion of less than 99%. The calculated mass activity of m-CuO-150 (0.199 mol h⁻¹ g⁻¹) was 2.6 times higher than that of the original catalyst, m-CuO, and this value was 1.2 times higher than that of m-Cu-250 (0.166 mol h⁻¹ g⁻¹). However, as the reduction temperature increased to 350 °C, m-Cu-350 exhibited a drastic decrease in activity with severe collapse of the Cu particles, along with evidence of reduction of the BET surface area. Fig. 6b shows the surface normalized reaction rate over the series of m-CuO catalysts at various reduction temperatures. The overall surface normalized activity followed a trend similar to the mass activity; however, the surface activity of the m-CuO-150 and m-Cu-250 catalysts was much higher than those of the original catalyst (m-CuO) and m-Cu-350. To determine the real active sites for FAL hydrogenation on the m-CuO series, the specific Cu⁺ surface fraction obtained from the DRIFT spectra (Fig. 6b, right axis). The resulting values (×10⁻³) are as follows: 17.9, 16.0, 16.2, and 13.4 mol h⁻¹·(Cu⁺ fraction⁻¹) for m-CuO, m-CuO-150, m-Cu-250, and m-Cu-350, respectively (Table S4). The calculated reaction rates have similar values with slight deviations. When the rate of m-Cu-350 reduced by the in situ H2 environment is normalized by the Cu⁺ fraction, the resulting value (×10⁻³) is 17.0 mol h⁻¹·(Cu⁺ fraction⁻¹). It demonstrates that the concentration of exposed Cu⁺ determines the overall activity of the catalyst. There has been much controversy in the literature concerning the catalytic mechanism related to the active site (Cu⁺ or Cu° species) for catalytic hydrogenation [11,18,51]. Rao et al. reported that Cu⁺ species functioned as the active site for FAL and crotonaldehyde hydrogenation [12]. Vargas-Hernandez et al. showed that the presence of both Cu⁺ and Cu° species on the surface of the SBA-Cu catalyst provided high activity and selectivity for the conversion of FAL to FA [11]. Rao et al. also suggested that both Cu⁺ and Cu° sites were required for optimal performance in the hydrogenation of FAL to FA [13]. However, the way in which Cu⁺ changes the properties of metal catalysts has not yet been fully elucidated and is controversial in the literature. In this study, m-CuO-150, which has the highest fraction of Cu⁺, showed the highest activity among the evaluated catalysts. Although m-CuO-150 has a mixed Cu²⁺ and Cu° phase, it indicates that Cu⁺ is heavily involved in the catalytic cycle and the Cu° site is more important than the Cu⁺ or Cu²⁺ site for FAL hydrogenation. Fig. 6c shows the change in the FAL conversion and selectivity for the m-CuO-150 catalyst as a function of the reaction temperature (120–180 °C). As the reaction temperature increased from 120 to 180 °C, the FA conversion increased from 9 to 99% with high FA selectivity (89–94%). However, when the reaction was performed at high temperature (180 °C), the FA selectivity dropped from 94 to 79%, indicating that decarbonylation of FAL was preferred to produce FR at higher temperature.

3.4. Discussion

Calculations and experiments were combined to investigate the adsorption and migration behavior of hydrogen (step 2). H migration on the Cu₂O(100) surface was evaluated from NEB calculation [30]. Herein, calculations for the Cu(111) and CuO(100) surface were excluded because of the low adsorption energy of FAL and the lack of adsorption of molecular H₂, respectively. Initially, the H₂ molecule,
which approaches the Ovac site on the Cu2O(100) surface, leaves two pre-dissociated H atoms (H1‒H2), as shown in Fig. 2e and 7a. Another H (third hydrogen, H3) was attached and recombined with H2. The total binding energy of all three hydrogens on the Cu2O(100) surface is shown Fig. 7a. The Cu2O(100) surface is composed of Cu–O chains. The H2 atom can migrate from its initial position to another Ovac site along the perpendicular direction of the Cu–O chain, shown as intermediate states I (full dissociation), II, and III (migrations) in Fig. 7a. The largest energy barrier of 0.64 eV was found for the transition between I and II. The H migration barrier of 0.64 eV was the highest during FAL hydrogenation, indicating it is a rate-determining step for the FAL hydrogenation process. To experimentally identify the activation barrier for hydrogen migration, H2-TPD was used. Because H2-TPD indicated the desorption of a trace of H2 at ~250 K for the Cu surface with a H2 binding energy of 0.81 eV [39], the H2-TPD of m-CuO was evaluated at low temperature (~160 K). Fig. 7b shows the H2-TPD spectra at different heating rates of 2, 5, 10, and 15 K⋅min−1 under a constant flow of pure He (50 mL⋅min−1). As the heating rate (β) increased, the peak maximum shifted to slightly higher temperature. From the Kissinger equation, the slope of the ln(β/Tmax) vs. 1/Tmax plot represents the activation energy of H2 divided by the gas constant R [40]. Therefore, the experimental activation energy for H2 adsorption on Cu2O was 0.559 eV. This was determined from the linear plot of the H2-TPD data (Fig. 7c); the value is in good agreement with the theoretical prediction of hydrogen migration (0.64 eV). Based on the reaction mechanism of FAL hydrogenation consisting of 3 steps, the Cu2O(100) surface is much more preferable than the Cu(111) and CuO(100) surfaces in consideration of FAL adsorption, adsorption, dissociation, and migration of hydrogen.
4. Conclusion

In order to investigate the active sites of Cu-based catalysts for FAL hydrogenation, DFT calculations were performed in combination with catalytic experiments. Comparison of the adsorption of FAL and H2 on the Cu(111), CuO(100), and Cu2O(100) surfaces showed that the Cu2O (100) surface has the highest adsorption energy for FAL, indicating that FAL has the highest reaction potential. For H2 adsorption and dissociation, the CuO(100) surface had a negligible barrier for the adsorption of H2 molecules for which the dissociation energy was weak, compared to the CuO(100) surface with a strong binding energy for H2. For the catalytic experiment, various m-CuO derived catalysts were prepared under controlled reduction conditions. Reduced m-CuO underwent a sequential transformation (CuO → Cu2O → Cu) to produce Cu2+ , Cu+, and Cu- phases on the surface. Overall, the activity for FAL hydrogenation was proportional to the concentration of exposed Cu+ in the m-CuO catalysts with high selectivity for FA. The calculated energy for hydrogen migration (0.64 eV) was in good agreement with the H2 binding energy obtained from the H2-TPD experiment (0.559 eV). The catalytic experiments. Comparison of the adsorption of FAL and H2 on the Cu surfaces and nanorows, Surf. Sci. 646 (2016) 221–229.


