Hydrogenation of methyl laurate to produce lauryl alcohol over Cu/ZnO/Al$_2$O$_3$ with methanol as the solvent and hydrogen source*

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Abstract: Hydrogenation of methyl laurate was conducted over a Cu/ZnO/Al$_2$O$_3$ catalyst, using methanol as the solvent and hydrogen source, to give lauryl alcohol. In this process, the solvent underwent partial decomposition in contact with the catalyst to generate hydrogen, which served as the hydrogenation agent. The effect of different factors on the reaction was examined, to optimize production of lauryl alcohol with high conversion efficiency and selectivity. Use of methanol as the solvent not only favored the reaction, but also suppressed a side reaction involving transesterification between methyl laurate and lauryl alcohol. Under optimal reaction conditions, 91.8 % conversion of methyl laurate and 88.8 % yield of lauryl alcohol could be achieved.

Keywords: Cu/ZnO/Al$_2$O$_3$; heterogeneous catalysis; hydrogenation; lauryl alcohol; methanol; methyl laurate; supercritical fluids.

INTRODUCTION

Fatty alcohols derived from renewable resources, such as plant oils and animal oils, have found their numerous applications in industries, mostly used as raw materials for the synthesis of surfactants or plasticizers [1,2]. Especially, the fatty-alcohol-based surfactants have gained growing significance in the detergent market in the past few years, owing to their excellent washing properties and superior biodegradability compared to conventional detergents made from petrochemicals [3]. Commercially, fatty alcohol can be produced by one of three processes: the Ziegler process, the Oxo process, or high-pressure hydrogenation of fatty acids or esters. The former two processes utilize petrochemical feedstock derived from fossil resources, whereas the fatty acids or esters used in the latter process can be obtained from the transesterification between fats and methanol (methanolysis) or the hydrolysis of fats [4–7]. To ensure a high degree of product safety for consumers and the environment, renewable resources have often shown advantages over the petrochemical raw materials, and could therefore be regarded as the ideal raw material basis. The importance of natural fatty acid or ester process is steadily growing relative to the alternative petrochemical processes [8].

Catalyst is crucial in the hydrogenation of fatty acids or esters to produce fatty alcohols. Since Cu-containing catalysts allow for selective hydrogenation of the C–O double bond and are relatively inactive in carbon–carbon double-bond hydrogenation, they are used in the hydrogenation of the esters

or acids [9]. In 1931, Adkins reported a Cu–Cr (copper–chromium) catalyst for hydrogenation of ethyl ester [10]. The Cu–Cr-based catalysts are frequently used in the hydrogenation of fatty ester and result in high activity and alcohol yield [11–13]. However, the use of Cr as promoter is not environmentally benign because of the releasing of hazardous Cr during the catalyst preparation. Researchers therefore studied the replacement of Cr with Zn [14–17], Mn [18], Fe [19], or other promoters [20–22]. As one of the best Cr-free catalysts, Cu–Zn-based catalysts are widely used in the industrial production of natural fatty alcohols in the world [14–17]. Besides, some catalysts based on noble metals, such as Ru and Pd, have been studied with regard to obtaining the fatty alcohol by hydrogenating the fatty esters and acids [23–28].

Besides being applied in the hydrogenation of fatty acids or esters to produce fatty alcohols, Cu–Zn-based catalysts have been widely used in the hydrogenation and dehydrogenation processes. The $Cu/ZnO/Al_2O_3$ catalysts are traditionally used for low-temperature water–gas shift reaction and methanol synthesis [29–33], steam reforming of methanol to produce hydrogen [34,35], catalytic fixation of CO_2 to methyl formate or dimethylformamide [36,37], and gas-phase hydrogenation of maleic anhydride to γ-butyrolactone [38–42]. $Cu/ZnO/Al_2O_3$ catalyst prepared with coprecipitation method exhibits high activity for methanol conversion and hydrogen production in the steam reforming of methanol at a low temperature [34].

Typically, hydrogenation of fatty acids or esters to produce fatty alcohol is carried out under high hydrogen pressures between 20 to 30 MPa, and high temperatures ranging from 573 to 673 K [9–14]. Under such conditions, the poor solubility of hydrogen in the liquid phase, which leads to a lack of hydrogen on the catalyst surface, limits the reaction. The mass transfer resistance can be reduced by using a supercritical solvent, and the reaction is carried out at homogeneous conditions. As a consequence, the reaction rates are orders of magnitude higher than those carried out in the traditional two-phase process [43–46]. Based on this concept, van den Hark and Härröd [43] used propane (C_3H_8) as a supercritical solvent for the homogeneous hydrogenation of fatty acid methyl esters. The reaction rate was 500 times higher than those obtained in the traditional two-phase process.

Supercritical methanol has been utilized for the transesterification of the vegetable oils without the catalysts, and high conversions (80–100 %) were obtained [47–52]. This is primarily because supercritical methanol and oil exist in a single phase [48,49,53]. To elucidate the phase behavior for the product mixture of the biodiesel production process, the vapor–liquid equilibria for methanol + fatty acid methyl ester system were measured at 493–543 K, near the critical temperature of methanol (T_c = 512.64 K) [54].

In the present work, we studied the hydrogenation of fatty acid methyl ester in methanol without adding hydrogen. The methyl laurate hydrogenation was conducted over $Cu/ZnO/Al_2O_3$ catalyst. The properties of the catalysts were characterized using transmission electron spectroscopy (TEM), scanning electron microscopy (SEM), X-ray powder diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) techniques. The effects of different factors, such as the molar ratio of methanol to methyl laurate, reaction temperature, reaction time, and the molar ratio of Cu, Zn, and Al in the $Cu/ZnO/Al_2O_3$ catalyst were examined. Under optimal reaction condition, methyl laurate could be converted to lauryl alcohol with high conversion and selectivity. It is not necessary to add hydrogen into the system in the presence of methanol. Methanol partially decomposed over $Cu/ZnO/Al_2O_3$ catalyst to produce hydrogen, which was used for the hydrogenation of the methyl laurate. There are three advantages to this reaction system: (1) using methanol as the solvent favors the reaction; (2) the reaction conducted under low pressure is safe, and the equipment to supply hydrogen in the previous process is not necessary; (3) the side reaction involving transesterification between methyl laurate and lauryl alcohol is suppressed in the presence of methanol.

RESULTS AND DISCUSSION

The effect of methanol and water

The influences of the molar ratio of methanol, water, and methyl laurate on the hydrogenation of methyl laurate were studied. Figure 1 shows the effect of the molar ratio of methanol to methyl laurate on the conversion of methyl laurate, and the yield and selectivity of lauryl alcohol. It is demonstrated that methyl laurate can be hydrogenized effectively to produce lauryl alcohol over $Cu/ZnO/Al_2O_3$ catalyst in the presence of methanol. The amount of methanol added has an effect on the conversion and selectivity. As the molar ratio of methanol to methyl laurate was lower than 15, the conversion was about 65 %. The conversion decreased to 35 % when the molar ratio increased to 20. When the molar ratio increased from 5 to 15, the yield and selectivity of lauryl alcohol increased from 33 to 63 % and 50 to 95 %, respectively. In addition to the hydrogenation of methyl laurate (1), there is an important side reaction (2) in the system. Methanol is the product of the transesterification between methyl laurate and lauryl alcohol. Raising the amount of methanol restrained the side reaction, resulting in the increase in the yield and selectivity of lauryl alcohol.
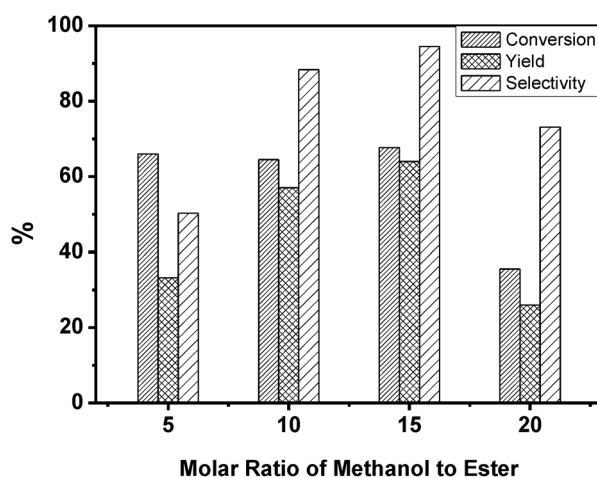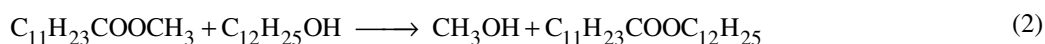
$$C_{11}H_{23}COOCH_3 + H_2 \xrightarrow{\text{Cat}} C_{12}H_{25}OH + CH_3OH \tag{1}$$

$$C_{11}H_{23}COOCH_3 + C_{12}H_{25}OH \longrightarrow CH_3OH + C_{11}H_{23}COOC_{12}H_{25} \tag{2}$$

Fig. 1 The effect of the molar ratio of methanol to methyl laurate on the reaction. Reaction conditions: methyl laurate: 2 mmol; methanol: 2 × (5, 10, 15, 20) mmol; $Cu/ZnO/Al_2O_3$ (3:2:2): 50 mg; temperature: 515 K; reaction time: 20 h.

It is known that water can enhance the methanol conversion in the steam reforming of methanol for hydrogen production, where the main products are hydrogen and carbon dioxide as well as a minor product, carbon monoxide (eqs. 3 and 4). In this work, we investigated the influence of the amount of water on the hydrogenation of methyl laurate. As shown in Fig. 2, the presence of a small amount of water can enhance the conversion of methyl laurate and the yield of lauryl alcohol. When the molar ratio of water to methyl laurate was lower than 2, the selectivity for lauryl alcohol did not change. But the conversion, yield, and selectivity decreased when the molar ratio of water to methyl laurate was higher than 2. Huang et al. [16] have investigated the effect of water on Cu/ZnO catalyst for hydrogenation of methyl laurate. The results indicated that catalytic activity decreased with increased amount of water in

methyl laurate. It was found that the main reason for the Cu/ZnO catalyst deactivation was the water occlusion of active catalytic sites that resulted from the low solubility of water in the substrate and the promotion of crystal growth, as well as the Cu/ZnO catalyst agglomeration in the presence of water. The recycle of the catalyst Cu/ZnO/Al$_2$O$_3$ (3:2:2) showed that the yield of lauryl alcohol decreased to 70.3 % in the fourth run. The decrease of the activity may result from the reasons cited above. In this reaction system, the optimal amount of water was two equivalent moles of the methyl laurate.
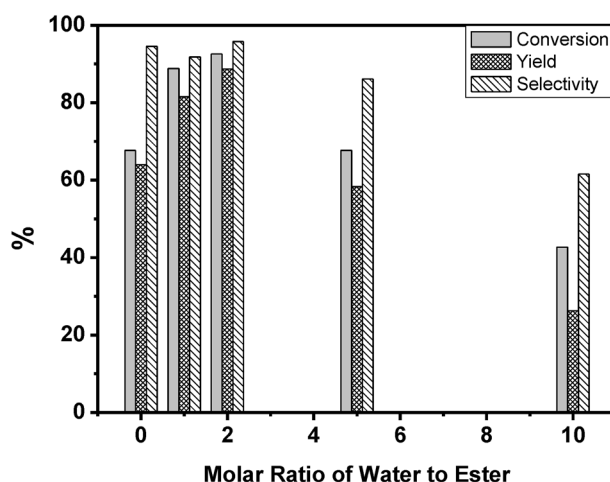
$$CH_3OH \xrightarrow{\text{Cat}} 2H_2 + CO \qquad (3)$$

$$CO + H_2O \xrightarrow{\text{Cat}} H_2 + CO_2 \qquad (4)$$

Fig. 2 The effect of the molar ratio of water to methyl laurate on the reaction. Reaction conditions: methyl laurate: 2 mmol; methanol: 30 mmol; water: 2 × (0, 1, 2, 5, 10) mmol; Cu/ZnO/Al$_2$O$_3$ (3:2:2): 50 mg; temperature: 515 K; reaction time: 20 h.

The effect of reaction conditions

We evaluated the effect of reaction time on the conversion, yield, and selectivity of the reaction when the molar ratio of methanol, water, and methyl laurate was 15:2:1. The results are presented in Fig. 3. The conversion, yield, and selectivity increased with the increasing reaction time. At 15 h, the conversion and selectivity exceeded 91 and 96 %, respectively. The methyl laurate conversion and alcohol selectivity did not change after 15 h.

As shown in Fig. 4, the reaction temperature has a significant influence on the activity of the Cu/ZnO/Al$_2$O$_3$ catalyst. Below 515 K, the conversion of methyl laurate and yield of alcohol were less than 80 %. Only 32 % conversion and 24 % yield were obtained at 493 K. The yield increased with temperature in the range of 493 to 515 K. The conversion of 91.8 % and yield of 88.8 % were achieved at 515 K. The conversion and selectivity did not change with the further increase of the reaction temperature above 515 K.
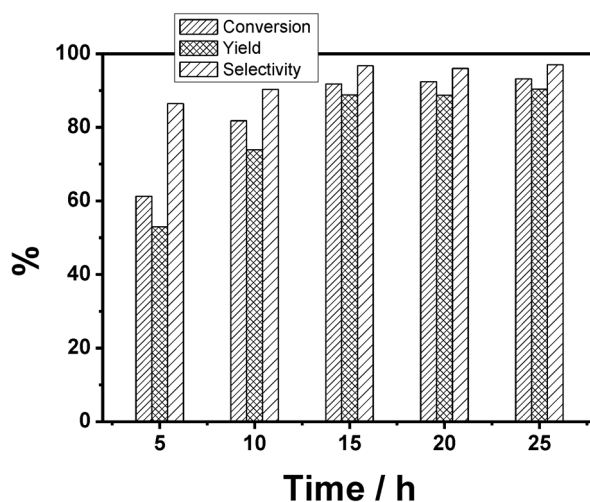
Fig. 3 The effect of reaction time on the reaction. Reaction conditions: methyl laurate: 2 mmol; methanol: 30 mmol; water: 4 mmol; Cu/ZnO/Al$_2$O$_3$ (3:2:2): 50 mg; temperature: 515 K.
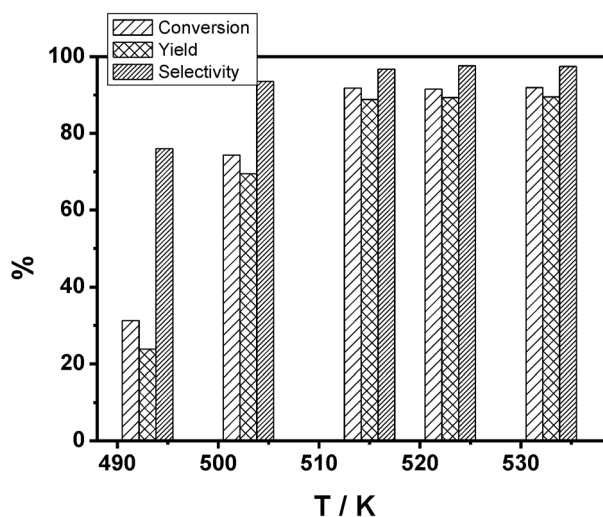

Fig. 4 The effect of reaction temperature on the reaction. Reaction conditions: methyl laurate: 2 mmol; methanol: 30 mmol; water: 4 mmol; Cu/ZnO/Al$_2$O$_3$ (3:2:2): 50 mg; reaction time: 15 h.

The effect of catalyst composition

Table 1 shows the dependence of the conversion, yield, and selectivity on the molar ratio of Cu, Zn, and Al in Cu/ZnO/Al$_2$O$_3$ catalyst and catalyst dosage. It can be observed that the conversion, yield, and selectivity did not change noticeably when the same amount of Cu element was used in the reaction (entries 1–5). When the same amount of catalysts with different molar ratio was used (entries 2, 6–9), the conversion, yield, and selectivity decreased with the decrease in the amount of Cu in the catalyst, indicating that Cu is the active component for the hydrogenation of methyl laurate in Cu/ZnO/Al$_2$O$_3$ catalyst [9].

Table 1 Effect of the content of Cu, Zn, and Al in Cu/ZnO/Al$_2$O$_3$ and the catalyst dosage on the reaction.

Entry	Molar ratio of Cu:Zn:Al	Catalyst/ mg	Conversion/ %	Yield/ %	Selectivity/ %
1	4:1:2	36	91.2	89.5	98.1
2	3:2:2	50	91.8	88.8	96.7
3	2.5:2.5:2	61	91.0	90.0	98.9
4	2:3:2	78	91.4	90.3	98.9
5	1:4:2	162	91.2	90.2	98.9
6	4:1:2	50	92.2	88.9	96.4
7	2.5:2.5:2	50	90.8	88.3	97.2
8	2:3:2	50	89.3	81.8	91.6
9	1:4:2	50	76.0	61.8	81.3

Reaction conditions: methyl laurate: 2 mmol; methanol: 30 mmol; water: 4 mmol; reaction temperature: 515 K; reaction time: 15 h.

Catalyst characterization

The Cu/ZnO/Al$_2$O$_3$ (3:2:2) catalyst was characterized with SEM, TEM, XRD, and XPS techniques. The results are presented in Fig. 5. The morphology of the surface particles of Cu/ZnO/Al$_2$O$_3$ catalyst samples is shown in Fig. 5a. The catalyst particles with diameters of about 20–50 nm aggregated into
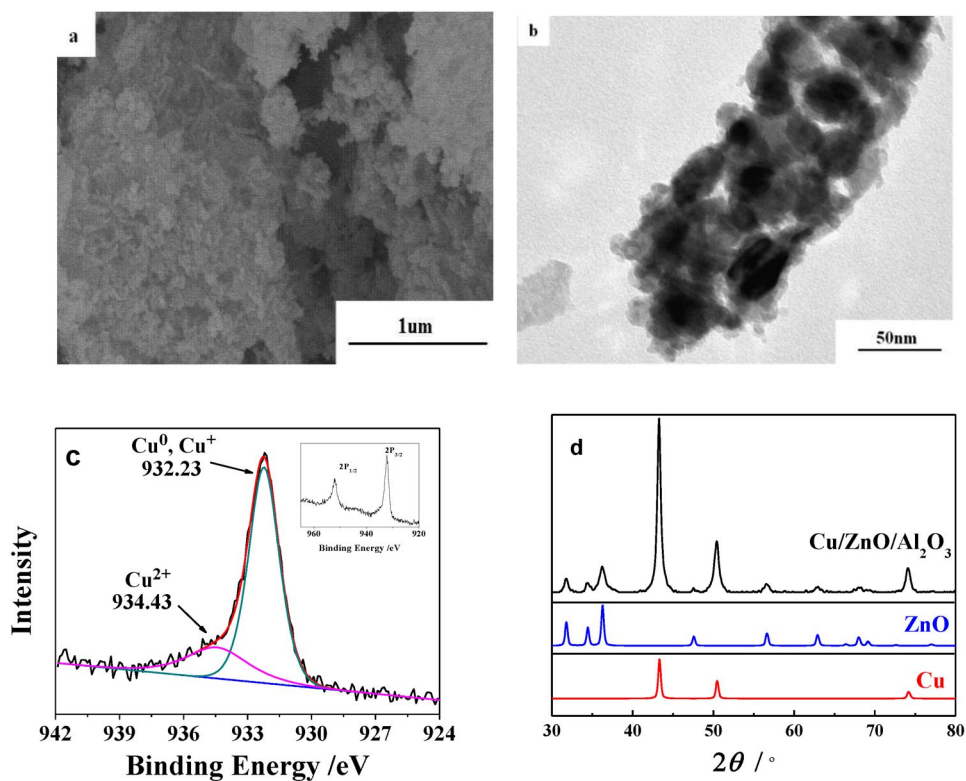

Fig. 5 Characterization of the catalyst Cu/ZnO/Al$_2$O$_3$ (3:2:2) SEM image (a), TEM image (b), XPS spectrum (c), and XRD pattern (d).

larger particles (Fig. 5b). Cu nanoparticles were arranged in an alternating fashion with ZnO. The Cu component existed in the form of Cu(0), as evidenced by XPS (Fig. 5c) spectrum, and XRD (Fig. 5d) pattern. A small peak for Cu^{2+} could be observed in the XPS spectrum, which may be attributed to the partial oxidation of the metal after exposure in air. The sizes of the Cu nanoparticles calculated from the XRD pattern were in the range of 15–25 nm.

Methanol decomposition and the utilization efficiency

During the hydrogenation of methyl laurate, no hydrogen was added to the reaction system. Methanol decomposed to hydrogen and carbon monoxide (eq. 3). The hydrogenation took place in methanol, which served as both the solvent and hydrogenation source. The amount of methanol decomposed and the hydrogen utilization efficiency in the hydrogenation of methyl laurate at some reaction conditions are listed in Table 2. Under the same reaction conditions, the amount of decomposed methanol increased with the prolonged reaction time. During the reaction, about 10 % of methanol decomposed to hydrogen and carbon monoxide. The hydrogen utilization efficiency in the hydrogenation of methyl laurate under different conditions was higher than 50 %.

Table 2 Methanol decompositions and the hydrogen utilization efficiency.

Reaction time/h	Conversion of methyl laurate/%	Amount of decomposed methanol/mmol	Ratio of methanol decomposed to initially added/%	Utilization efficiency of hydrogen/%*
10	81.8	2.91	9.2	50.7
15	91.8	3.18	10.0	55.7
20	92.3	3.36	10.5	52.9

Reaction conditions: methyl laurate: 2 mmol, methanol: 30 mmol, water: 4 mmol, reaction temperature: 515 K.
*Utilization efficiency of hydrogen is the ratio of hydrogen used for hydrogenation of methyl laurate to the hydrogen produced from methanol decomposition.

CONCLUSIONS

The methyl laurate hydrogenation is performed over $Cu/ZnO/Al_2O_3$ catalyst using methanol as the solvent and hydrogen source. $Cu/ZnO/Al_2O_3$ is an effective catalyst for the hydrogenation of methyl laurate and the decomposition of methanol to produce hydrogen. The reaction conditions, the amount of methanol and water, and the composition of the catalyst have a significant effect on the reaction. The conversion of methyl laurate and the selectivity for lauryl alcohol can be higher than 90 and 98 %, respectively. There are three advantages for this reaction system. Firstly, hydrogen has good solubility in methanol. Using methanol as solvent could reduce the mass transfer resistance, which is a crucial problem in fatty acid ester hydrogenation. Secondly, methanol can decompose to produce hydrogen on $Cu/ZnO/Al_2O_3$ catalyst, and it is not necessary to add hydrogen into the system. Therefore, the equipment is simple and safe. Thirdly, the presence of methanol can restrain the side reaction, i.e., the transesterification between methyl laurate and the product lauryl alcohol.

EXPERIMENTAL

Materials

$Cu(NO_3)_2 \cdot 3H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$ were purchased from Sinopharm Chemical Reagent Co. Ltd. $Al(NO_3)_3 \cdot 9H_2O$, Na_2CO_3, *n*-octanol, methyl laurate, and methanol were provided by Beijing Chemical Reagent Company. All chemicals were analytical grade and used as received.

Methods

The SEM examination was conducted on a Hitachi-s4800 electron microscope operated at 10 kV. The samples were spray-coated with a thin layer of platinum before observation. The transmission electron microscopy (TEM) characterization was carried out on JEM 2011 at an accelerating voltage of 100 kV. The samples were dispersed in ethanol and dropped on a carbon film supported on Cu grid for TEM analysis. Powder XRD measurements were performed on a Rigaku D/max2500 diffractometer using CuKα radiation (λ = 1.5406 Å). XPS data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W AlKα radiation. The base pressure was about 3×10^{-9} mbar. The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon. The ratios of the metals in the catalysts were calculated from the mass of the chemicals used to prepare the catalysts, which agreed well with the data determined in this work by ICP (ICP-OES, Optima 5300DV). This is understandable because the precursors of Cu, Zn, and Al are insoluble at the pH value to prepare the catalysts.

Catalyst preparation

The catalyst Cu/ZnO/Al$_2$O$_3$ was prepared using a commonly used coprecipitation method. In the experiment, Cu(NO$_3$)$_2$·3H$_2$O (4.4 g), Zn(NO$_3$)$_2$·6H$_2$O (3.6 g), and Al(NO$_3$)$_3$·9H$_2$O (4.8 g) were dissolved in 500 mL of water. Then an aqueous solution of Na$_2$CO$_3$ (0.25 mol L^{-1}) was added dropwise at a rate of 1 mL min^{-1} under stirring at 353 K until pH = 7. The resulting precipitate was aged for 4 h. The suspension was filtered and washed several times with distilled water to remove the NaNO$_3$. The solid was dried at 393 K overnight, and then calcined in air at 623 K for 12 h. The catalyst was reduced at 573 K for 3 h with hydrogen and cooled to 373 K in a hydrogen flow (20 mL min^{-1}). Then the catalyst was cooled to room temperature in a nitrogen flow (30 mL min^{-1}). The other catalysts were prepared by similar procedures using the corresponding materials.

Catalytic reaction

The methyl laurate hydrogenation was carried out in a stainless steel batch reactor of 6.5 mL, which was similar to that used previously [55]. Typically, 0.05 g of catalyst, 0.43 g of methyl laurate, 0.96 g of methanol, and 0.072 g of H$_2$O were charged into the reactor. The reactor was heated to the desired temperature by air bath. Then the stirrer was started. After a certain time, the reactor was placed in ice water and the gas was released slowly. A known amount of internal standard n-octanol was then added to the reactor. The reaction mixture was transferred into a glass tube, and the catalyst was separated by centrifugation. The quantitative analysis of the reaction mixture was conducted using a GC (Agilent 6820) equipped with a flame ionization detector (FID) and a PEG-20M capillary column (0.25 mm in diameter, 30 m in length).

   In the reaction system, besides the hydrogenation of methyl laurate, the transesterification between methyl laurate and the produced lauryl alcohol took place as a side reaction, as shown in eq. 2. The conversion of methyl laurate and the yield of lauryl alcohol are calculated using eqs. 5 and 6.

$$\text{Conversion}\left(\%\right) = \frac{n\left(\text{methyl laurate}\right) - m\left(\text{methyl laurate}\right)}{n\left(\text{methyl laurate}\right)} \tag{5}$$

$$\text{Yield}\left(\%\right) = \frac{m\left(\text{lauryl alcohol}\right) + m\left(\text{lauryl laurate}\right)}{n\left(\text{methyl laurate}\right)} \tag{6}$$

   Where n (methyl laurate) is the initial amount of moles of methyl laurate; m (methyl laurate) is the amount of moles of methyl laurate in the reaction system at the end of reaction; m (lauryl alcohol)

is the amount of moles of product lauryl alcohol in the reaction system; *m* (lauryl laurate) is the amount of moles of byproduct lauryl laurate in the reaction system. The selectivity for lauryl alcohol can be calculated from the ratio of yield of lauryl alcohol to the conversion of methyl laurate.

ACKNOWLEDGMENTS

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