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Effect of water on Cu/Zn catalyst for hydrogenation of fatty methyl ester to fatty alcohol

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Abstract−The effect of water on Cu/Zn catalyst prepared by co-precipitation for hydrogenation of methyl laurate in a slurry phase was studied using a stirred autoclave reactor system. The catalysts were characterized by means of XRD, BET, H_2-TPR, SEM and TEM. The results indicate that catalytic activity decreases with increased amount of water in methyl laurate. Correlating with the results from the above characterization, it is found that the main causes for the water deactivation of the Cu/Zn catalyst were the water occlusion of active catalyst sites by the low solubility of water in the substrate and the promotion of crystal growth, as well as the Cu/Zn catalyst agglomeration in the presence of water.

Key words: Fatty Alcohol, Cu/Zn Catalyst, Deactivation, Water

INTRODUCTION

Natural fatty-alcohols derived from renewable resources, such as plant oils and animal oils, have become the important base feedstock for the production of cationic, anionic and nonionic surfactants, e.g., fatty alcohol sulfates, ether sulfates, ethoxilates and alkyl polyglucosides [1,2]. These fatty-alcohol-based surfactants have also gained more growing significance in the detergent market during the past few years, due to their excellent washing properties and superior biodegradability compared to conventional detergents made from petrochemicals [3].

Commercially, fatty alcohols can be produced by one of three processes: the Ziegler process, the Oxo process, or by a high pressure hydrogenation of fatty acids or esters. The latter process is the only process that uses natural fats or oils as raw materials, whereas the first two processes utilize petrochemical feedstocks [4-7]. To ensure a high degree of product safety for consumers and the environment, renewable resources have often been shown to have advantages when compared with petrochemical raw materials, and could therefore be regarded being the ideal raw material basis. The importance of nature fatty acids or esters process is steadily growing relative to the alternative petrochemical processes [8].

Normally, copper-containing catalysts are suitable for hydrogenation of esters to alcohols, since they allow for selective hydrogenation of carbon-oxygen bonds and are relatively inactive in carbon-carbon hydrogenolysis [9]. Copper on itself, however, is usually not active, sinter-resistant and mechanically stable enough for industrial operation, so promoters are usually added to obtain the desired chemical and physical properties [9]. As early as in 1931, Adkins [10] discovered a copper-chromium (Cu/Cr) catalyst for hydrogenation of ethyl ester. Similar catalysts are still frequently used for hydrogenation of fatty ester [11-15]. Nowadays, however, the catalysts containing chromium are not environmentally benign because of the releasing of environmental hazard Cr^{6+} in the process of the Cu/Cr catalyst preparation. Research is therefore focused on the replacement of chromium by zinc [16], manganese [17], iron [18] and other promoters [9,19,20]. Cu/Zn catalyst is the commonly used one in those catalysts.

The natural oils, e.g., coconut oil, and palm kernel oil, are the best options of the raw materials for the preparation of fatty alcohol. However, natural oils always contain impurities which are harmful for the catalyst activity and difficult to be removed from fatty esters. Some of the impurities are from the plant growing process, some from the usage of pesticides [5], and some from the process of fatty ester preparation. Even a trace of these impurities in the feedstock may act as the catalyst poison, which would cause catalyst deactivation and shorten the life of the catalyst, e.g., the life of Cu/Zn catalyst for fatty alcohols preparation is about 3 to 6 months. Little is known about the nature of the impurities present in feedstocks and deactivation mechanism of the impurities to the Cu/Zn catalyst except for those discussed by Voeste [5].

Examples of catalyst poisons in the hydrogenation process of fatty ester to fatty alcohol may be water, soaps, fatty acids, glycerin and glycerides. Works [21-23] have been carried out for nature of the reaction inhibition caused by those compounds. Controversies still remain concerning the effect of water on the activity of the catalyst. In some references [23,24], the catalyst was put in the reactor, and reduced in the reactor. The authors suggested that the presence of water inhibited the reduction of catalyst to its active form and blocked active sites by occlusion which resulted in lower activity of the catalyst, while others [21] showed that water had no influence on the catalyst activity.

Water could be brought into fatty esters through the washing process of fatty ester purification. It is obviously important to know how the water influences the Cu/Zn catalyst. The aim of this study

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is to gain further insight in the effect of water on Cu/Zn catalyst prepared by co-precipitation for hydrogenation of fatty methyl ester to fatty alcohol. The hydrogenation of methyl laurate was taken as a model reaction.

EXPERIMENTAL

1. Catalyst Preparation

The Cu/Zn catalyst was prepared by parallel co-precipitation method according to the literature [25]. Mole ratio of Cu:Zn for the final synthesis catalyst was 1.5. After dissolving 21.75 g $Cu(NO_3)_2 \cdot 3H_2O$ and 17.85 g $Zn(NO_3)_2 \cdot 6H_2O$ in 500 ml of de-ionized water, 200 ml of aqueous solution of 19 g Na_2CO_3 was added under vigorous stirring at 50 °C. The resulting precipitate was washed repeatedly with de-ionized water after the filtration of the suspension. After drying at 110 °C overnight, the solid was crushed and pelleted by adding 2 wt% of graphite. The pellet was reduced under 10 ml/min of hydrogen by heating to 240 °C at a rate of 5 °C/h and then cooled to room temperature under the atmosphere of hydrogen. The obtained catalyst was then transferred in nitrogen atmosphere and stored in methyl laurate before use.

2. Catalytic Reactions

Catalyst deactivation experiments were conducted in a 1-L stirred autoclave reactor. Experimental runs typically consisted of charging the reactor with about 400 g catalyst/ester slurry with a weight ratio of 0.025 and varying amount of water in methyl laurate, followed by raising the hydrogen pressure to about 4 MPa. The reactor temperature was then raised to 240 °C and the hydrogen pressure was increased to 21 MPa. After a 5 h reaction, the reactor was cooled to room temperature and the gas was released. Liquid samples were analyzed by a GC equipped with a flame ionization detector (FID). 1-octanol was used as the internal standard compound for analysis. All reactants were identified by Micromass GCTTM GC-mass spectroscopy.

The reaction equation can be generalized according to:

$$R\text{-}COOCH_3+2H_2 \rightarrow R\text{-}CH_2OH+CH_3OH \qquad (1)$$

In addition to the main reaction, there is an important side reaction. Transesters are intermediates and the formation is favored by the presence of the product alcohol [16]:

$$R\text{-}COOCH_3+R\text{-}CH_2OH \rightarrow R\text{-}CH_2OOCH_2\text{-}R+CH_3OH \qquad (2)$$

3. Catalyst Characterization

Powder X-ray diffraction (XRD) patterns were determined with a Rigaku D/Max 2550 VB/PC diffractometer (Japan) equipped with Cu/Kα (λ=0.154056 nm) radiation operating at 40 kV and 450 mA with 2θ ranging from 10° to 80° at a rate of 8°/min. The used catalyst after reaction was protected from oxidation with benzene and polystyrene. The crystal size of copper was calculated from the peak broadening by the Scherrer equation.

The nitrogen adsorption-desorption isotherms were measured on a Micromeritics ASAP 2010 analyzer (USA). The samples were degassed at 190 °C for 6 h to remove the gaseous impurities. The surface area was determined by adsorption of nitrogen at −196 °C. The pore volume and average pore diameter were calculated by the BET method. The pore size distributions were calculated with the BJH method on the desorption branch.

Temperature-programmed reduction (TPR) measurement was done on a Micromeritics AutoChem 2900 instrument (USA). The H_2-TPR was performed by passing 10% H_2/Ar (flowing rate=30 mL/min) on 0.2 g catalyst at a heating rate of 10 °C/min. The hydrogen consumption was monitored with a thermal conductivity detector (TCD).

SEM images were acquired in a JEOL JSM6360LV scanning electron microscope (Japan) operated at 15 kV.

TEM images were collected by using a JEOL JEM 2100 electron microscope with a LaB_6 filament as the source of electrons, operating at 200 kV.

RESULTS AND DISCUSSION

1. Elimination of the Diffusion

A series of batch hydrogenations of methyl laurate were performed with various agitation speeds. Fig. 1 shows the conversion of methyl laurate and selectivity of dodecanol as a function of the agitation speed. Under these reaction conditions, the external diffusion could be eliminated with an agitation speed over 600 rpm. Internal diffusion could also be eliminated as the impeller had crushed the catalyst to more than 200 mesh before the reaction started. Thus, in the present work, the agitation speed was chosen to be 750 rpm.

2. Catalytic Performance of Cu/Zn Catalyst Deactivated by Water

Various amounts of water were added in the run of hydrogenation of methyl laurate to investigate the influence of water on the activity of the Cu/Zn catalyst. Fig. 2 shows the conversion of methyl laurate and the selectivity of dodecanol as a function of the water concentration. As shown, a small amount of water presented in the reaction has a significant influence on both the conversion and the selectivity, e.g., when the concentration of water is increased from 0.1 to 2 wt%, the conversion decreases from 95% to 71%, and the selectivity decreases from 97% to 62%. Fully pre-reduced catalyst appears to be relatively immune to low levels of water contamination, e.g., 0.1 wt% of water in methyl laurate. Thakur [23] investi-

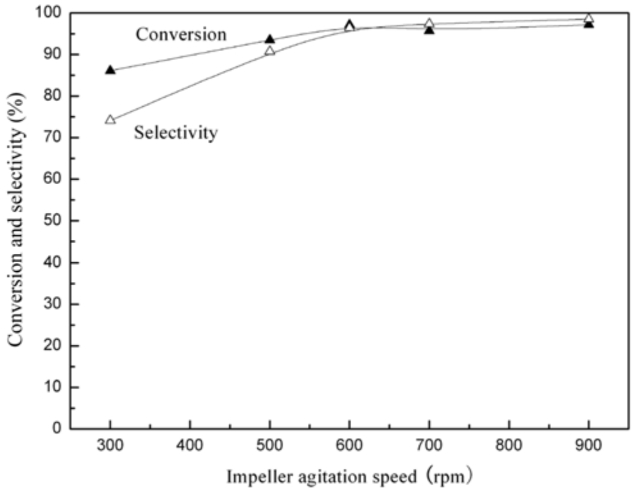


Fig. 1. Conversion of methyl laurate and selectivity of dodecanol at different impeller agitation speeds (reaction conditions: Cu/Zn catalyst, $m_{catalyst}/m_{methyl\ laurate}$=0.025, T=240 °C, P=21 MPa, t=300 min).

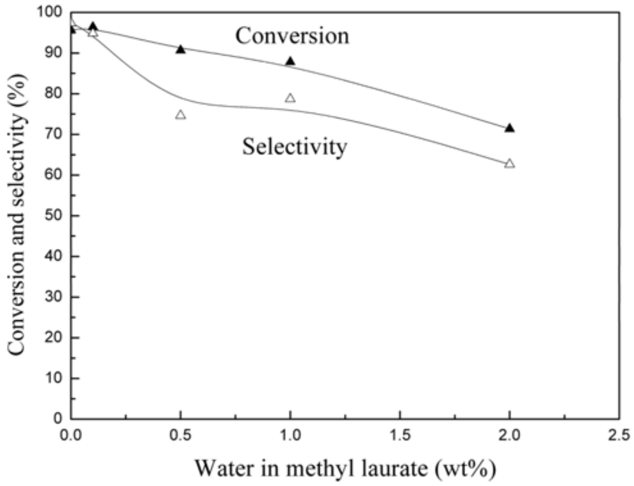


Fig. 2. Conversion of methyl laurate and selectivity of dodecanol at different levels of water in methyl laurate (reaction conditions: Cu/Zn catalyst, $m_{catalyst}/m_{methyl\ laurate}$=0.025, T=240 °C, P=21 MPa, t=300 min, n=750 rpm).

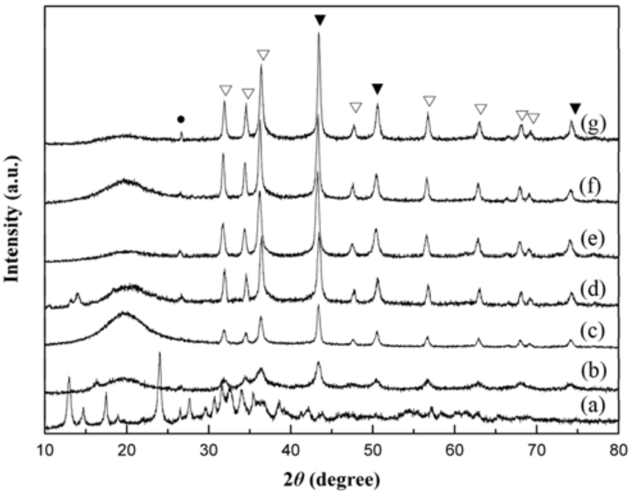


Fig. 3. XRD patterns of the Cu/Zn catalysts ((▼) Cu^0, (▽) ZnO, (●) C).

(a) unreduced; (b) reduced before reaction; (c) after reaction without adding water in methyl laurate; (d) after reaction with adding 0.1 wt% of water in methyl laurate; (e) after reaction with adding 0.5 wt% of water in methyl laurate; (f) after reaction with adding 1.0 wt% of water in methyl laurate; (g) after reaction with adding 2.0 wt% of water in methyl laurate

gated the effect of water on the deactivation of Cu/Cr catalyst in the reaction of batch hydrogenations of methyl laurate. It was reported that significant levels of water residing in the liquid phase effectively blocked the catalytic active sites. This may also explain the effect of water on the Cu/Zn catalytic activity.

3. Characterization of Catalysts

XRD patterns of Cu/Zn catalyst samples are shown in Fig. 3. Distinct diffraction peaks in Fig. 3(a) are assigned to basic zinc carbonate, $Zn(OH)_2(CO_3)_2$, and basic cupric carbonate, $Cu(OH)_2(CO_3)_2$, in the unreduced Cu/Zn samples. In Fig. 3(b)-(g), the obvious diffraction peaks assigned to Cu^0 and ZnO were detected in the other six reduced Cu/Zn catalyst samples, indicating that copper was highly dispersed in the catalysts and water had no influence on the valence state of the catalytic active site. The diffraction peak of C was also detected at 2θ=26.3° as graphite had been added in the catalyst preparation. The Scherrer equation was used to calculate the crystal size of Cu^0 from the peak at 43.5° for Cu(111). As shown in Table 1, the crystal size of Cu^0 was increased from 13.4 to 24.9 nm, corresponding to the reinforcing and narrowing of diffraction peaks of Cu^0 in Fig. 3(b)-(g), which may be due to the increasing amount of water added to the reaction. For the reduced Cu/Zn catalyst sample after reaction without water, the increment of Cu^0 crystal size, compared with that before reaction, may be due to the promotion by agglomeration, as the reaction temperature of 240 °C, much higher than copper's Hüttig temperature (179 °C) [26], can enable surface atoms of catalyst to become significantly mobile.

The textural properties of the catalysts are also listed in Table 1. BET surface area of the Cu/Zn catalyst samples varied with the amount of water in methyl laurate. It is found that the variation of surface area has the same trend with that of the Cu/Zn catalytic activity, indicating that the surface area has a significant effect on the catalytic performance in the present case. Furthermore, for the reduced catalysts, the surface areas of used catalysts are all smaller than that of the fresh one, suggesting that the increment of particle size during the activity evaluation leads to the deactivation of the Cu/Zn catalysts.

H_2-TPR profiles of the Cu/Zn catalyst samples are illustrated in Fig. 4. The Fig. 4(a) curve of the unreduced Cu/Zn catalyst has two peaks; according to references [27-29], the low-temperature reduction peak and high-temperature reduction peak of the unreduced

Table 1. Physical properties and Cu^0 crystal size of the Cu/Zn catalysts

Cu/Zn catalysts	S_{BET} m^2/g	Pore volume ml/g	Average pore diameter nm	Crystal size (nm)[a]
				Cu(111)
Un-reduced	-	-	-	-
Reduced, before reaction	39.5	0.15	10.2	13.4
After reaction without water in methyl laurate	19.1	0.11	12.3	16.5
After reaction with 0.1 wt% of water in methyl laurate	16.8	0.07	17.2	17.1
After reaction with 0.5 wt% of water in methyl laurate	16.2	0.06	24.7	18.7
After reaction with 1.0 wt% of water in methyl laurate	15.8	0.04	26.5	20.2
After reaction with 2.0 wt% of water in methyl laurate	7.4	0.01	47.6	24.9

[a] Calculated from the peak at 43.5° for Cu(111) by the Scherrer equation

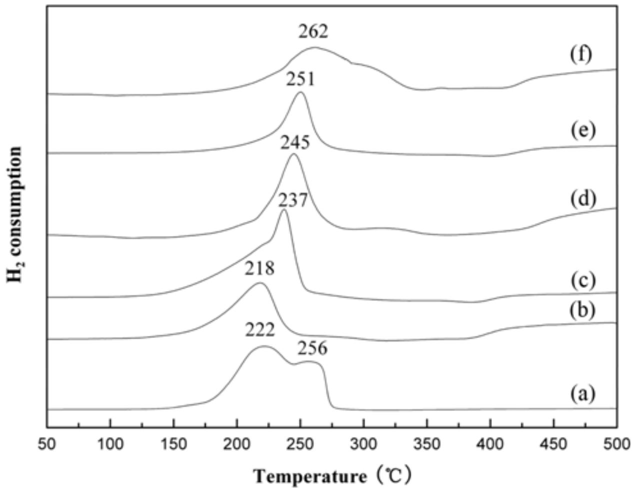


Fig. 4. H_2-TPR profiles of the Cu/Zn catalysts: (a) unreduced; (b) after reaction without adding water; (c) after reaction with adding 0.1 wt% of water in methyl laurate; (d) after reaction with adding 0.5 wt% of water in methyl laurate; (e) after reaction with adding 1.0 wt% of water in methyl laurate; (f) after reaction with adding 2.0 wt% of water in methyl laurate.

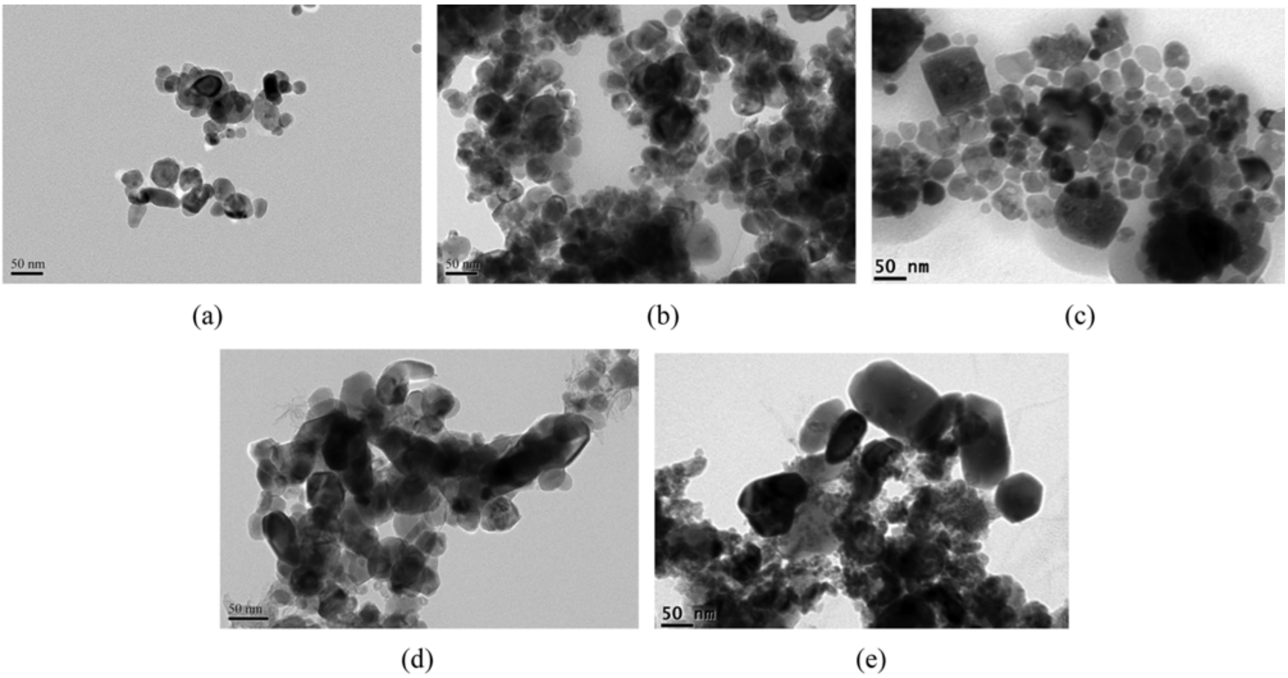
Cu/Zn catalyst are attributed to the reduction of highly dispersed CuO and that of bulk CuO, respectively. In Fig. 4(b)-(f), the position of the peak shifts to higher temperature gradually, from 218 to 262 °C, which is consistent with increasing amount of water in methyl laurate, from 0 to 2.0 wt%. Correlated to the catalytic activities, it is obvious to find that the variation of the reduction peak is well consistent with that of catalytic activity, indicating that the more difficult the reduction of the Cu/Zn catalyst, the less catalytic activity there is. This phenomenon may be explained by the fact that the aforementioned increase of copper crystallite size implies a more difficult reduction of Cu/Zn catalysts. The catalytic activity might be mainly affected by the size of reducible crystal; as the solubility of water in substrate is low, the catalytic surface would be rendered inactive by the accumulation of water, and the presence of water can also cause damage to the Cu/Zn catalyst by promotion of the crystal growth [30,31].

TEM images of the Cu/Zn catalyst samples are shown in Fig. 5. In Fig. 5(a), the TEM image of the used Cu/Zn catalyst without adding water in the reaction reveals the Cu crystallite sizes in the range of 14-35 nm, which is consistent with the results discussed earlier in Table 1. Cu crystallite sizes increases gradually, from 28-43 nm to 39-69 nm, and the agglomeration degree of Cu/Zn catalyst becomes higher, as the level of water in methyl laurate is increased from 0.1 to 2.0 wt%.

The morphology of the surface particles of Cu/Zn catalyst samples is shown in Fig. 6. The used catalyst without added water in reaction exhibits a homogeneous morphology of particles in Fig. 6(a). However, after reaction with adding 0.1 wt%, 0.5 wt% and 1.0 wt% of water in methyl laurate, the surface particles of the Cu/Zn catalyst grow bigger and obvious agglomerate appears in Fig. 6(b)-(d). After reaction with adding 2.0 wt% of water, the agglomeration became even worse, indicating that the Cu/Zn catalyst underwent agglomeration during the reaction and the agglomeration became more worse as water amount increased, confirming the TEM results.

CONCLUSIONS

The water deactivation of Cu/Zn catalyst prepared by co-precip-



(a) (b) (c)

(d) (e)

Fig. 5. TEM images of the Cu/Zn catalysts after reaction with adding various amount of water in methyl laurate.
(a) without adding water, d=14-35 nm; (b) 0.1 wt% of water, d=28-43 nm; (c) 0.5 wt% of water, d=34-49 nm; (d) 1.0 wt% of water, d=30-53 nm; (e) 2.0 wt% of water, d=39-69 nm

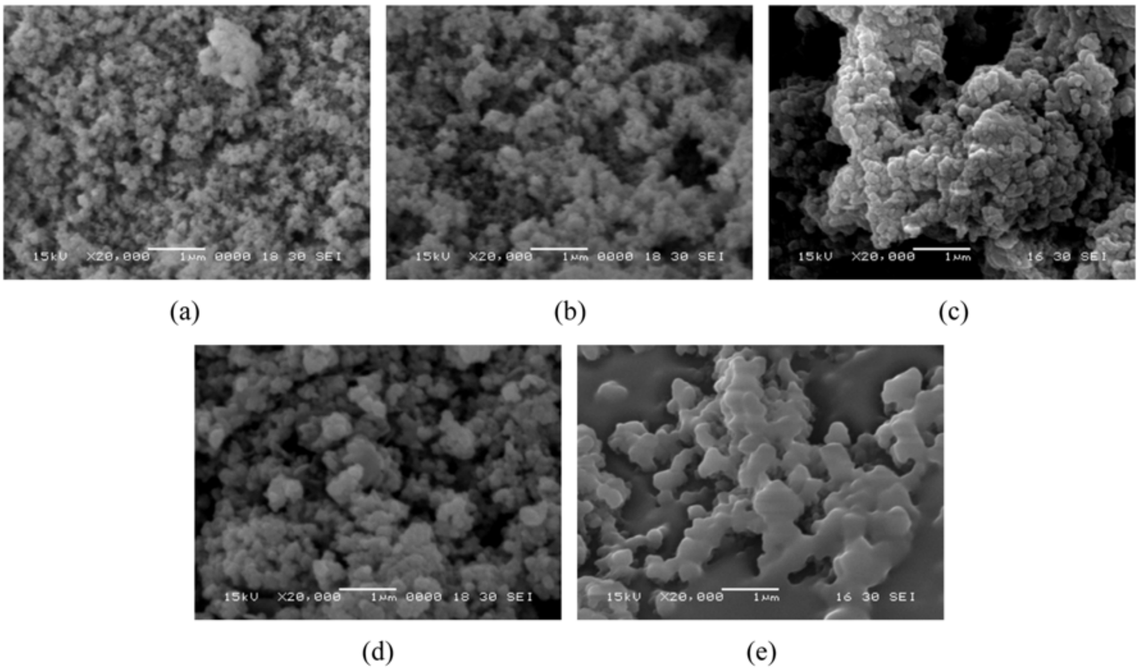


Fig. 6. SEM images of the Cu/Zn catalysts after reaction with adding various amount of water in methyl laurate.
(a) without adding water; (b) 0.1 wt% of water; (c) 0.5 wt% of water; (d) 1.0 wt% of water; (e) 2.0 wt% of water

itation was evaluated for hydrogenation of fatty methyl ester to fatty alcohol. The results indicate that the fully pre-reduced catalyst is relatively immune to low levels of water contamination. With increasing amount of water in methyl laurate, conversion and selectivity of the reaction are correspondingly reduced. By correlation of the results from catalyst characterization, it is found that the variation of catalytic activity of Cu/Zn catalyst is in very good agreement with that of the Cu^0 crystal size. The results of the present work implied that the main causes for the water deactivation of the Cu/Zn catalyst were the water occlusion of active catalyst sites by the low solubility of water in the substrate and the promotion of crystal growth, as well as the catalyst agglomeration in the presence of water.

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