Deactivation Mechanism of Cu/Zn Catalyst Poisoned by Organic Chlorides in Hydrogenation of Fatty Methyl Ester to Fatty Alcohol

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Abstract The mechanism of deactivation of Cu/Zn catalyst poisoned by organic chlorides in hydrogenation of methyl laurate to lauryl alcohol in a slurry phase was studied in a stirred autoclave. The catalyst was prepared by co-precipitation, and the un-poisoned and poisoned catalysts were characterized using XRD, BET, ICP-AES and SEM, respectively. The results indicated that both of catalytic activity and selectivity decreased with increasing amount of chlorides in methyl laurate. According to the characterization of the catalysts, the main causes for the chlorine deactivation of the Cu/Zn catalyst were that the chlorides could modify the valence state of active sites, decrease the BET surface area, and promote the growth of crystal and catalyst agglomeration. Further investigation indicated that chlorine atom decomposed from the chlorides combined with ZnO to produce ZnCl₂, which could be dissolved in the liquid and promote ester-exchange reaction to lauryl laurate as Lewis acid.

1 Introduction

Heterogeneous catalytic hydrogenation is of great industrial importance, where the solid catalyst is reasonably

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essential for this process. The performance of the catalyst is relying on its activity and/or selectivity, as well as the stability. However, catalyst deactivation is inevitable for most processes and the industrial expectation is to retain certain activity and selectivity for an acceptable time scale.

Over the past decades, researches on catalyst deactivation have been steadily developing, while literature addressing this topic has expanded considerably to include books [1, 2] and comprehensive reviews [3–6]. Deactivation can occur by a number of different mechanisms, both chemical and physical in nature. Those are commonly divided into five classes, namely poisoning, fouling, thermal degradation (sintering, evaporation) initiated by the often high temperature, mechanical damage and corrosion/leaching by the regenerated in some way, depending on the process used.

Fatty alcohols (FOH) and their derivatives have found their numerous applications in industries and constitute one of the largest groups within the oleo-chemicals, e.g., they are widely used as surfactants, lubricants, and additives in many industrial products [7, 8]. Commercially, fatty alcohols could be produced by one of three processes: the Ziegler process, the Oxo process, and heterogeneous catalytic hydrogenation of fatty acids or esters at a high pressure and suitable temperature. However, the latter process is the only process that uses natural fats or oils as raw materials whereas the first two processes utilize petrochemicals feedstocks [9–11]. To ensure a high degree of product safety for consumers and the environment, renewable biomass resources have often been shown to have more advantages than petrochemical raw materials and could therefore be regarded as the ideal raw material basis. The importance of nature fatty acids or esters process is steadily growing relative to the alternative petrochemical processes during these years.

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As early as in 1931, Adkins [12] discovered a copperchromium (Cu/Cr) catalyst for hydrogenation of ethyl ester. Similar catalysts are still frequently used for hydrogenation of fatty ester [13–15]. Nowadays, the catalysts containing chromium is not environmentally benign because of the releasing of environmental hazard Cr⁶⁺ in the process of the Cu/Cr catalyst preparation. Researches were therefore focused on the replacement of chromium by zinc [16], manganese [17], iron [18] or other promoters [19, 20]. Cu/Zn catalyst is the commonly used one among those catalysts. However, natural oils, the best alternative to the raw materials for preparation of FOH, always contain various impurities which are harmful to the catalyst performance and difficult to be removed from fatty esters. Some of the impurities are from the growing process of the plants or usage of pesticides, and others may from the process of fatty ester preparation [9, 21]. Even trace of these impurities in the feedstock may act as the catalyst poisons, which would cause catalyst deactivation and shorten the lives of the catalyst, e.g., typical operating lives of Cu/Zn catalysts in large plants varies from 3 to 6 months depending on the process concerned and the actual plant configuration [21, 22]. Catalyst deactivation is a problem of great and continuing concern in the practice of industrial FOH processes. Costs to industry for catalyst replacement and process shutdown total millions of dollars per year.

Chlorides are known to be a particularly virulent poison for Cu catalysts [4], and this is important with catalysts for the low-temperature water–gas shift reaction. In practice, the only halide usually encountered in hydrogen and ammonia plants is chloride in the form of HCl. To the best of our knowledge, little is known about the nature of the chlorides present in fatty methyl ester feedstocks prepared from natural fats and oils, possible candidates are monoand dialkyl chlorides [23–25].

In this work, the effects of mono- and dialkyl chlorides on the physical and chemical properties of Cu/Zn catalyst, prepared by co-precipitation method, were investigated. This kind of information is of pivotal importance for the design of deactivation-resistant catalysts, the operation of industrial chemical reactors, and the study of specific reactivating procedures. The hydrogenation of methyl laurate to dodecanol was taken as a model reaction.

2 Experimental

2.1 Catalyst Preparation

The copper zinc catalyst was prepared by parallel co-precipitation method according to the literature [21]. Mole ratio composition used to give the final synthesis catalyst is Cu:Zn = 3:2. After dissolving $Cu(NO_3)_2 \cdot 3H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$ in 500 mL of de-ionized water, a desired amount of aqueous solution of 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 overnight drying at 110 °C, 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 dodecyl methyl ester before use.

2.2 Catalytic Reactions

Catalyst deactivation experiments were carried out in a 1-L stirred autoclave reactor. The experimental conditions, such as the effects of agitation rate, reaction time, catalyst load in FAME, reaction temperature, and hydrogen pressure were systematically optimized during preliminary tests. Results indicated that mass transfer resistance could be eliminated with an agitation rate over 600 rpm, the best performance of Cu/Zn catalyst could be reached at the reaction temperature of 240 °C and at the hydrogen pressure of 21 MPa, and the conversion of methyl laurate, as well as the selectivity of methyl laurate to lauryl alcohol, increased with reaction time (from 0 to 5 h) and catalyst added in FAME substrate (from 0 to 2.5 wt%), respectively, and then kept stable with further increment of reaction time and catalyst load in FAME. Therefore, 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 chlorides, followed by purging the autoclave three times with hydrogen and raising the pressure to about 4 MPa. The reactor temperature was then raised to 240 °C and the hydrogen pressure was increased to 21 MPa with continuous supply of hydrogen. After reaction with the agitation of 750 rpm for 300 min, the heater was removed and the temperature decreased rapidly with the reactor cooled to room temperature, then the gas was released slowly. The liquid samples were analyzed by a GC equipped with a flame ionization detector (FID), where 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:

 $R-COOCH_3 + 2H_2 \rightarrow R-CH_2OH + CH_3OH$ (1)

where R represents $CH_3(CH_2)_{10}$.

$$x = \frac{1 - w_1}{1 + \frac{4w_1}{214.38}}$$
$$s = \frac{\left(1 + \frac{x}{214.38} \times 4\right) \times w_2}{\frac{x}{214.38} \times 186.34}$$

In addition to the main reaction, there is an important side reaction. Transesters are intermediates and the formation is favoured by the presence of the product alcohol [16], and this was justified by Takanori et al. [26] that ester-exchange reaction occurred very easily and selectively without catalyst:

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

2.3 Catalyst Characterization

Powder X-ray diffraction (XRD) patterns were determined using a Rigaku D/Max 2550 VB/PC diffractometer (Japan) equipped with Cu/K α ($\lambda = 0.154056$ nm) radiation operating at 40 kV and 450 mA for 2 θ angles 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.

Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analyses were conducted on a Thermo Elemental IRIS 1000 instrument. The samples were dissolved by hydrochloric acid and nitric acid with a volume ratio of 3, and diluted with deionized water to a constant volume before detection.

The nitrogen adsorption–desorption isotherms were measured on a Micromeritics ASAP 2010 chemisorption analyzer (USA). The samples were degassed at 190 °C for 6 h to obtain a residual pressure of less than 10^{-5} Torr. The surface area was determined by adsorption–desorption of nitrogen at 77 K. The pore volume and average pore diameter were calculated using the BET method. The pore-diameter distributions were calculated using the BJH method on the desorption branch.

Scanning electron microscope (SEM) images were acquired in a JEOL JSM- 6360LV microscope operating at 15 kV.

3 Results and Discussion

3.1 Effect of Chlorides on the Catalytic Performance of Cu/Zn Catalyst

In the hydrogenation of methyl laurate to lauryl alcohol, the effect of chlorides on catalytic activity and selectivity of Cu/Zn catalyst was investigated. Figures 1 and 2 show the conversion of methyl laurate versus chlorine concentration, and the selectivity of methyl laurate to lauryl alcohol versus chlorine concentration, respectively, under different kinds of model chlorides, e.g., 1,2-dichloroethane (DCE), 1-chlorododecane (CD), 1,1,2-trichloroethane (TCE), and 1-chlorobutane (CB). As shown in Fig. 1, the chlorine concentration increases from 0 to 0.2 mmol/g_{catalyst}, resulted in slight decrease of the conversion of methyl laurate. Thereafter, the conversion of methyl laurate sharply decreases from about 90–20% with the increasing chlorine concentration, from 0.2 to 0.5 mmol/g_{catalyst}. The poisoning effects of chlorides on the conversion of methyl laurate are more and more serious with the increase of the chlorine concentration of chlorides, and the toxicity order is CB > TCE > CD > DCE.

As shown in Fig. 2, the selectivity of lauryl alcohol decreased slightly at first, from 97% to about 85%, and then sharply, from about 85% to about 20%, with the chlorine concentrations increasing from 0 to 0.5 mmol/ g_{catalyst}. According to reference [27], as the lauryl alcohol generation decreases with increasing contaminant level, so follows the generation of the fatty-fatty ester, the appearance of its maximal level increasingly delayed. Behavior of this system is similar to hydrogenations under unfavorable thermodynamic conditions, i.e., low H₂ pressure or low temperature. Therefore, intermediate docecyl dodecanoate generation and suppression of its depletion by hydrogenation leading to the decreasing selectivity of lauryl alcohol. The poisoning effects of chlorides on the selectivity of lauryl alcohol are more and more serious with the increase of the chlorine concentration of chlorides, and the toxicity order is also CB > TCE > CD > DCE.



Fig. 1 The conversion of methyl laurate versus chlorine concentration with different chlorides: (1) DCE; (2) CD; (3) TCE; (4) CB (reaction conditions: Cu/Zn catalyst, $m_{\text{catalyst}}/m_{\text{methyl laurate}} = 0.025$, T = 240 °C, P = 21 MPa, t = 300 min, n = 750 rpm)



Fig. 2 The selectivity of lauryl alcohol versus chlorine concentration with different chlorides: (1) DCE; (2) CD; (3) TCE; (4) CB (reaction conditions: Cu/Zn catalyst, $m_{\text{catalyst}}/m_{\text{methyl}}$ laurate = 0.025, T = 240 °C, P = 21 MPa, t = 300 min, n = 750 rpm)

Earlier XPS studies on the deactivation of Cu/Zn catalyst by alkylthiols in our group have revealed that low concentration alkylthiol could bonded with Zn^{2+} on the surface of the Cu/ZnO catalyst as a form of Zn-SR and the molecular toxicity increased continuously with the chain length of alkylthiols. According to reference [28], the poisoning effects of alkylthiols on the activity of Cu/Zn catalyst are more and more serious with the increase of the alkyl chain of alkylthiols. However, this is not the case for chlorides, and the toxicity of alkyl chlorides didn't increase with the chain length by comparison of CD and CB in the present work. Heldal and Mørk [23, 24] have carried out a comprehensive investigation of the reaction of alkyl chlorides over various copper catalysts, such as copper chromite, copper-on-silica and Raney copper hydrogenation catalysts, a dehydrohalogenation with the formation of corresponding alkene and adsorbed chlorine was found to take place. However, those results also failed to explain the difference of toxicity between CD and CB with a same concentration. In view of the above discussion, the possibility that the Zn component of copper catalyst may play a vital role in the chlorine deactivation of Cu/Zn catalyst cannot be entirely excluded. Moreover, the bond dissociation energy difference between $Cl-nC_4H_9$ (84.5 \pm 1.0 kcal/mol) and Cl-nC₁₂H₂₅ (73.4 kcal/mol) may also suggest the difference of the performance of the Cu/Zn catalyst poisoned by CB and CD, respectively.

3.2 Characterization of the Catalysts

Figure 3 shows XRD patterns of Cu/Zn catalyst samples poisoned by different chlorides, where that of used catalyst without poison was also shown. It could be seen from



Fig. 3 XRD patterns of different Cu/Zn catalyst samples, poisoned by: (1) no chloride; (2) 0.2 mmol/g_{catalyst} Cl of DCE; (3) 0.3 mmol/ $g_{catalyst}$ Cl of CD; (4) 0.5 mmol/ $g_{catalyst}$ Cl of TCE; (5) 15 mmol/ $g_{catalyst}$ Cl of CB

Fig. 3 that diffraction peaks of Cu^0 , ZnO, and Cu_2O were detected for the Cu/Zn catalysts poisoned by 0.2, 0.3, and 0.5 mmol/g_{catalyst} chlorides (Fig. 3(2–4)). Figure 4 shows the diffraction patterns of Cu/Zn catalysts poisoned by different concentration of CD. With the same chlorine concentration, diffraction peaks of different chlorides are the same, which are not shown in Figs. 3 and 4. By comparison the peaks of poisoned catalysts to that of un-poisoned catalyst (Fig. 3(1)), it could be concluded that the existence of low concentration of chlorides could modify the valence state of the catalyst active site Cu^0 to Cu^{1+} (as Cu_2O). However, the expected ZnCl₂ or CuCl were not detected in the catalysts of Fig. 3(2–4) and Fig. 4(1–3), this



Fig. 4 XRD patterns of different Cu/Zn catalyst samples, poisoned by different chlorine concentrations of CD: (1) 0.2 mmol/ $g_{catalyst}$; (2) 0.3 mmol/ $g_{catalyst}$; (3) 0.5 mmol/ $g_{catalyst}$; (4) 15 mmol/ $g_{catalyst}$

may attribute to the XRD characterization limitation of the lower concentration or absence of those compounds on the catalysts. So, further increment of chlorine concentration of chlorides was introduced to the system to eliminate the problem in the XRD determination caused by the low concentration of the poison. As Fig. 3(5) and Fig. 4(4) show, when the concentration of chlorine increased to 15 mmol/g_{catalyst}, only Cu⁰ and CuCl were detected and the expected ZnCl₂ was else not existed, while Cu₂O disappeared in the XRD pattern.

Element analysis was carried out by ICP-AES and the results, shown in Table 1, indicate that the existence of chlorides causes the loss of Zn composition from the Cu/Zn catalyst, as the mole ratio of Cu to Zn increases from 1.5365 to 1.6307, with the chlorine concentration of chlorides increases from 0 to 0.5 mmol/g_{catalyst}. At the excess chlorine concentration of 1-chlorododecane (15 mmol/g_{catalyst}), this ratio further increases to 24.9131. Moreover, the liquid of the reaction mixture after the Cu/Zn catalyst deactivated by 15 mmol/g_{catalyst} 1-chlorododecane was also analyzed by ICP-AES, trace Cu and 0.913wt% of Zn are found, which indicates that Zn component of Cu/Zn catalyst could be leached into the liquid phase of the reactant by forming ZnCl₂ with chlorides.

From the species both in the liquid (e.g., n-dodecane in the liquid of the reaction mixture after the Cu/Zn catalyst poisoned by CD) and on the catalyst, we can suggest the possible reaction with the existence of chlorides besides the main reaction (1) and side reaction (2). The chlorine atom was decomposed from the chloride, e.g., CD, in the atmosphere of hydrogen in this case, see Scheme 1.

Scenario 1: Low $[Cl^-]$ Migration of Cl^- from Cu to ZnO:

$$2\mathrm{Cl}^{-} + \mathrm{ZnO} \longrightarrow \mathrm{ZnCl}_{2} + \mathrm{O}^{2-}$$
(i)

Migration of O^{2-} to Cu lattice:

$$2Cu + O^{2-} \longrightarrow Cu_2O$$
 (ii)

Scenario 2: High [Cl⁻]

$$\mathrm{H^{+}+Cl^{-}+CH_{3}OH} \longrightarrow \mathrm{CH_{3}O^{+}H_{2}+Cl^{-}}$$
(iii)

Table 1	Element	analysis	of the	Cu/Zn	catalysts
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Catalyst	<i>n</i> (Cu): <i>n</i> (Zn)
Blank run	1.5365
0.2 mmol/g _{catalyst} CD	1.5937
0.3 mmol/g _{catalyst} CD	1.6121
0.5 mmol/g _{catalyst} CD	1.6307
15 mmol/g _{catalyst} CD	24.9131





$$2CH_3O^+H_2 + 2Cl^- + ZnO \longrightarrow ZnCl_2 + 2H_2O + 2CH_3OH$$
(iv)

$$\begin{array}{cccc} 2\mathrm{Cu} + \mathrm{O}^{2-} & \longrightarrow & \mathrm{Cu}_2\mathrm{O} + 2\mathrm{H}^+ + 2\mathrm{Cl}^- & \longrightarrow & 2\mathrm{Cu}\mathrm{Cl} + \mathrm{H}_2\mathrm{O} \\ & & & & (\mathrm{v}) \end{array}$$

Under low [Cl⁻], reaction (i) is allowed thus permitting O^{2-} migration to Cu lattice forming Cu₂O (Fig. 3(2), (3) and (4)). When [Cl⁻] becomes higher, reaction (iii) becomes predominant and tends toward near complete consumption of ZnO (iiv). High [Cl⁻] also allows some CuCl to form possibly consecutively from Cu₂O (Fig. 3(5)).

Apart from those mechanisms discussed above, the poisoning effects of chlorides on the Cu/Zn catalyst may also have some relationship with the crystal size and BET surface area of the catalysts. As shown in Table 2, the crystal size of the Cu/Zn catalysts, poisoned by chlorides, are all larger than that of blank test (16.5 nm). Besides, the crystal size is increase with the the chlorine concentration of chlorides, from 0.2 to 15.0 mmol/gcatalyst. According to reference [4], the chloride poisoning of Cu catalysts can operate by following parallel mechanisms: the low melting point and high surface mobility of CuCl (430 °C) mean that even extremely small amounts of copper chloride are sufficient to provide mobile species that accelerate the sintering of Cu catalysts; ZnO reacts to form ZnCl₂, which also have low melting points (283 °C), and causes further poisoning and sintering of the catalyst. The physical parameters of the catalysts poisoned by different chlorides

Table 2 Physical property of the Cu/Zn catalysts

mmol/g _{catalyst}	Crystal size (nm) ^a Cu(111)			BET surface area (m ² /g)				
	DCE	CD	TCE	CB	DCE	CD	TCE	CB
0	16.5	16.5	16.5	16.5	19.1	19.1	19.1	19.1
0.2	19.0	19.6	24.3	26.5	-	-	-	_
0.3	20.1	21.1	26.3	29.3	-	-	-	-
0.5	21.2	23.1	30.7	33.2	10.9	6.3	4.9	3.6
15.0	30.3	31.2	32.3	34.4	0.28	0.18	0.10	0.04

 $^{\rm a}$ Calculated from the peak at 43.5° for Cu(111) by the Scherrer equation

are summarized in the last four columns of Table 2. The samples show a clearly decrease in the BET surface area as compared with un-poisoned Cu/Zn catalyst. The decrease in those parameters may be caused by the increment of the crystal size. The BET surface areas of the CD poisoned catalysts (e.g., 6.3 m²/g for 0.5 mmol/g_{catalyst} CD and 0.18 m²/g for 15 mmol/g_{catalyst} CD) are lower than that of the un-poisoned catalyst (e.g., 19.1 m²/g), also suggesting that the poisoning effects of chlorides on the activity of Cu/Zn catalyst are more and more serious with the increase of the chlorine concentration of chlorides. These results are also suggested by the XRD results and are further confirmed by the SEM results. As shown in Fig. 5, un-poisoned catalyst exhibits a homogeneous morphology of surface particles in Fig. 5a. However, after the Cu/Zn catalyst was poisoned by 0.5 mmol/gcatalyst of chlorides, the surface particles of the poisoned Cu/Zn catalysts grow bigger and obvious agglomeration appears in Fig. 5b-e, and the agglomeration get more worse as chlorine concentration increases to 15 mmol/gcatalyst (Fig. 5f-i), indicating that the Cu/Zn catalyst undergo agglomeration during the reaction and the agglomeration get more worse as chlorine concentration of chlorides increases. Figure 6 gives out a more visual observation of the agglomeration, the catalyst is in the state of powders with no reaction with chlorides, while obvious particles are formed in the case that the catalyst was poisoned by 15 mmol/ $g_{catalyst}$ CD.

Taking the above information into consideration, it could be concluded that, once the lauryl alcohol formed, it desorbed from the catalyst and then easily formed the lauryl laurate by the ester-exchange reaction. Therefore, for further lauryl alcohol formation, this lauryl laurate must be hydrogenated. As the BET surface area and the average pore diameter decrease with the increment of chlorine concentration of chlorides, the diffusion of the lauryl laurate into the smaller pores of catalyst is slow, resulting in slower rate of hydrogenation and consequently lower luaryl alcohol selectivity. The ester-exchange reaction could also possibly be catalyzed by ZnCl₂. Aqueous ZnCl₂ is known to be a strong Lewis acid. Thus, ZnCl₂ in presence of methanol may work as a weak Lewis acid. While the loss of conversion can be explained by the loss of accessibility to active sites (due to reduced surface area, crystal growth and agglomeration), the drastic loss of selectivity can also



Fig. 5 SEM images of Cu/Zn catalyst samples: poisoned by a no chloride; b-e 0.5 mmol/gcatalyst Cl of CD, CB, DCE, TCE; f-i 15 mmol/ gcatalyst Cl of CD, CB, DCE, TCE



Fig. 6 Digital images of Cu/Zn catalyst samples: poisoned by a no chloride; b 15 mmol/g_{catalyst} Cl of CD

be attributed to increase of $ZnCl_2$ concentration as more Zn are leached into the liquid phase, which promote esterexchange reaction to laury laurate and thus lower selectivity to lauryl alcohol.

4 Conclusions

The poisoning effects of chlorides on the activity of methyl laurate hydrogenation over Cu/Zn catalyst were studied in a stirred autoclave reactor under the conditions of T = 240 °C, P = 21 MPa, n = 750 rpm, $m_{catalyst}/m_{methyl laurate} = 0.025$, t = 300 min. The results indicate that the poisoning effect of chlorides become more serious with the increment of chlorine concentration, ranging from 0 to 0.5 mmol/ $g_{catalyst}$. Correlation to the XRD, BET, SEM and ICP-AES characterization results, it is found that the existence of chlorides could modify the valence state of active sites on the Cu/Zn catalyst, decrease the specific surface area of the Cu/Zn catalyst, agglomeration, as well as the loss of Zn composition of the Cu/Zn catalyst.

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