Hydrogenation of Ethyl Acetate to Ethanol over Bimetallic Cu-Zn/SiO2 Catalysts Prepared by Means of Coprecipitation

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A series of bimetallic Cu-Zn/SiO2 catalysts were prepared via thermal decomposition of the as-synthesized CuZn(OH)4(H2SiO3)2·nH2O hydroxides precursors. This highly dispersed Cu-solid base catalyst is extremely effective for hydrogenation of ethyl acetate to ethanol. The reduction and oxidation features of the precursors prepared by coprecipitation method and catalysts were extensively investigated by TGA, XRD, TPR and N2-adsorption techniques. Catalytic activity by ethyl acetate hydrogenation of reaction temperatures between 120 and 300 °C, different catalyst calcination and reduction temperatures, different Cu/Zn loadings have been examined extensively. The relation between the performance for hydrogenation of ethyl acetate and the structure of the Cu-solid base catalysts with Zn loading were discussed. The detected conversion of ethyl acetate reached 81.6% with a 93.8% selectivity of ethanol. This investigation of the Cu-Zn/SiO2 catalyst provides a recently proposed pathway for ethyl acetate hydrogenation reaction to produce ethanol over Cu-solid base catalysts.

Key Words : Cu-Zn/SiO2, Hydrogenation, Ethyl acetate, Ethanol

Introduction

Recently, there is an increasing interesting on using ethanol-gasoline as an alternative fuel.1,3 As a fuel for spark-ignition engines, ethanol has some advantages over gasoline, such as better anti-knock characteristics and the reduction of CO and UHC emissions.4,5 Although alcohol has these advantages, due to limitations in the technology, economic and regional considerations, still it can’t be used extensively.

Ethyl acetate (EA), as the downstream product of the acetic acid, is widely used both as a versatile solvent and as a raw material for organic synthesis. Besides the classical Fischer esterification process, the Tishchenko process6 and addition of acetic acid to ethylene using clay and heteropoly acid7-9 as a catalyst have been recently commercialized in Germany and Japan to produce EA. Studies of Cu/Zn/Al catalysts in ethanol dehydrogenative process to ethyl acetate have been focused on in recent years while ethanol is first dehydrogenated to acetaldehyde and then reacts with another ethanol or ethoxide species to form a hemiacetal, which is then dehydrogenated to ethyl acetate.10-12 A very promising alternative to the established processes is the single stage hydrogenation of ethyl acetate since ethyl acetate can be produced at lower cost and on a large scale by new processes, such as acetaldehyde condensation or ethylene and acid addition now. Processes which include the hydrogenation of ester hydrogenation reactions to form ethylene over Cu catalysts are the most promising. Recently, some Cu-containing catalysts for the hydrogenation of ethyl acetate were developed by Yang and coworkers.16,17

Highly dispersed Cu catalysts show good activity and selectivity in a series of catalytic hydrogenation reactions that are employed to selectively convert C=O groups13 hydrogenation of furfural to furfuryl alcohol containing other functional groups, such as C-OH bonds.14,15 In addition, highly dispersed copper catalysts are used to reduce carboxylic acid groups (-COOH) to produce alcoholic functionalities (-COH), e.g. in the reduction of lactic acid to 1,2-propane diol.16

As early as in 1931, Folksers and Adkins17 first described the reaction that Catalytic hydrogenation of esters to two alcohols using copper-chromium catalyst [Eq. (1)],

\[\text{R1COOR2+2H2} \rightarrow \text{R1CH2OH+R2OH} \] (1)

where R1 represents an alkyl group and R2 represents another alkyl group or hydrogen. Since Copper containing catalysts allow for selective hydrogenation of ester group (-COO-) and are relatively inactive in C-C bond hydrogenation, they are suitable for hydrogenation of esters to alcohols. Copper without additives is usually not active, sinter-resistant and mechanically stable enough for industrial operation. The additive chromium in Cu catalysts was frequently used for fatty ester hydrogenation.18-20 However, The use of chromium poses environmental problems since process water containing highvalence chrome (Cr5+, Cr6+) are generated during catalyst manufacture and regeneration. Research is therefore focused on the development of chromium-free catalysts for the hydrogenation of esters. Moreover, the addition of other metal oxide, such as ZrO2, Fe3O4 or ZnO221-23 has been extensively investigated to promote the activity of Cu in ester hydrogenation reaction.

For ester hydrogenation, few open literatures have focused
on the study of catalysts for ethyl acetate hydrogenation to alcohol [Eq. (2)]. In literatures studied on hydrogenation of aliphatic esters, the conversion of ethyl acetate was 40% while ethanol selectivity was 80%.^{26,27}

\[
\text{CH}_3\text{COOC}_2\text{H}_5 + 2\text{H}_2 \rightarrow 2\text{C}_2\text{H}_5\text{OH} \tag{2}
\]

In our work, we studied the selective hydrogenation of EA to ethanol on Cu-Zn/SiO\textsubscript{2} Catalysts using continuous fixed-bed reactor in mild reaction conditions. Catalysts with different Cu/Zn Molar ratios supported on silica were synthesized and tested for reaction system. These catalysts were characterized by N\textsubscript{2}-adsorption, X-ray diffraction (XRD), thermogravimetric (TG), temperature-programmed reduction with H\textsubscript{2} (H\textsubscript{2}-TPR). Over the most-active catalyst, a systematic study of the hydrogenation reaction, including the influence of reduction temperature, reaction temperature and reaction pressure, was carried out. Moreover, the effects of catalysts calcination temperature have been investigated. The main aim of this article is to determine the Cu-Zn/SiO\textsubscript{2} Catalysts activity on ethyl acetate hydrogenation. From these results, an explanation was formulated for the catalysts structure and role Zn on affecting the activity of Cu-Zn/SiO\textsubscript{2} catalysts.

**Experimental**

**Catalyst Preparation.** Hydrogenation components Cu-Zn/SiO\textsubscript{2} (Cu/Zn molar ratio = 3:1, 2:1, 1:1, 1:2, 1:3) were prepared by a new coprecipitation method. In a round bottom flask with distilled water, Na\textsubscript{2}SiO\textsubscript{3}·9H\textsubscript{2}O dissolved with stirring. To an aqueous solution containing appropriate amount of Cu(NO\textsubscript{3})\textsubscript{2}:5H\textsubscript{2}O, Zn(NO\textsubscript{3})\textsubscript{2}:4H\textsubscript{2}O (all chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd.) added and dissolved at room temperature. The copper-zinc nitrate solution was added dropwise to the vigorously stirred solution of sodium silicate over a period of 1 h. During the precipitation of the stirrer speed increased continuously.

After completion of the precipitation, the suspension was stirred for five minutes, filtered and washed three times with 350 mL of distilled water. The drying of the filter cake is carried out under atmospheric pressure at a temperature of 80°C for 12 h. The products were analyzed by gas chromatography-mass spectroscopy (GC-MS). The isotherms could be used to calculate the specific surface area (S), micro pore volume (V\textsubscript{mic}), total pore volume (V\textsubscript{t}), average micro pore size (L\textsubscript{mic}).

**X-ray Diffraction:** X-ray diffraction (XRD) technique was used to characterize the crystal structure. The experiments were performed using a Siemens D500 diffractometer, using Cu K\alpha radiation (40 kV, 100 mA) and equipped with a graphite monochromator with a reflected beam. The powder diffraction patterns were recorded in the 2θ range from 10° to 80°. An X-ray chamber-reactor was used for the high-temperature registration of the spectra. Preceding the experiments, 100 mg catalysts of different calcination temperatures were prepared.

**Temperature-Programmed Reduction:** Temperature programmed reduction (TPR) of H\textsubscript{2} was carried out on Auto Chem 2910 (Micromeritics) instrument to study the reducibility of Cu-Zn/SiO\textsubscript{2} catalysts. In a typical experiment, 0.05 g of calcined catalyst was exposed to a reducing gas consisting of 5.0 vol % H\textsubscript{2} in argon with a temperature ramp from ambient temperature to 900°C at a heating rate of 10°C/min.

**Thermo-gravimetric Analysis:** Thermo-gravimetric (TG) curves were obtained using a TA Instruments thermal analyzer. The samples were subjected to increased temperature, up to 700°C, at a rate of 10°C/min, while the nitrogen flow rate was held constant at 100 mL/min.

**Catalytic Test:** The reaction was performed in a fixed-bed reactor (Figure 1) operated in the down flow mode at a pressure of 2 MPa. The reaction temperature was measured with a thermocouple that was in contact with the catalyst bed. The organic-feed consisted of EA (100%) and was fed into the reactor using a micro-syringe pump. For each experiment, 1.35 g of uncalcined catalyst (20-40 mesh) was loaded into the flow reactor. The catalyst was reduced in situ at atmospheric pressure with H\textsubscript{2} (flow rate of 30 cm\textsuperscript{3}/min) in different temperature for 2 h. The products were analyzed using an Agilent 6890N gas chromatograph (flame ionization detector, HP-5 column, 30 m × 5 mm × 0.25 μm) and confirmed by gas chromatography-mass spectroscopy (GC-MS).

**Characterization of Catalyst.**

**N\textsubscript{2}-adsorption:** Nitrogen isotherms were measured at −196°C with an ASAP 2020 (Micromeritics). Before experiment, the samples were heated at 120°C and outgassed overnight at this temperature under a vacuum of 10\textsuperscript{-5} Torr.
Results and Discussion

Characterization of Pore Structure of Catalysts. Nitrogen adsorption-desorption isotherms of calcined (calcination temperature = 200 °C) Cu4Zn0Si4, Cu3Zn1Si4, Cu2Zn2Si4 and Cu1Zn3Si4 are shown in Figure 2. All of them are type IV pattern according to the IUPAC classification.28 The closure points of hysteresis loops of Cu4Zn0Si4 and Cu3Zn1Si4 located at a relative pressure of 0.6 and Cu1Zn3Si4 located at 0.4. However, the hysteresis loops of Cu2Zn2Si4 closed at 0.8, which suggested that the pore diameter increased with the amount of added Zn and reached highest when Cu/Zn molar ratio is 1:1. The calculated pore diameter of Cu4Zn0Si4, Cu3Zn1Si4, Cu4Zn0Si4 and Cu1Zn3Si4 were 3.59 nm, 3.75 nm, 4.10 nm and 3.43 nm, respectively. The calculated BET surface area of these catalysts decreased continuously from 282.29 m2/g (Cu4Zn0Si4) to 91.61 m2/g (Cu1Zn3Si4) with amount of added Zn (Table 1). These increases in pore diameter and decreases surface area could also be ascribed to that the orderliness of hydrotalcite-like CuZn(OH)4(H2SiO3)2·nH2O precursors declined with added Zn (see Figures 4 and 5).

TGA. Figure 3 shows the DTG profiles of as synthesized Cu4Zn0Si4 and Cu2Zn2Si4. TG profile of 3(a) indicates two major weight losses at around 50-150 °C and 180-250 °C, which can be identified as the losses of adsorbed surface water bound to gallery or external surfaces and H-bound water in interlayer.29 The overall weight loss of Cu4Zn0Si4 and Cu2Zn2Si4 from 30 °C to 550 °C is 36% and 35%, which was conformed with the formula of as-synthesize Cu(OH)2H2SiO3·nH2O and CuZn(OH)2(H2SiO3)2·nH2O.

XRD Analysis. The XRD analysis in Figures 4 and Figure 5 was carried out in order to identify the mineralogical structure of the Cu-Zn/SiO2 catalysts. The existence of diffraction reflections in the angle region indicates that samples had ordered structure on the micro pore scale. XRD patterns (see Figure 4 and 5) of all reduced samples showed characteristic reflections at 2θ = 43.30-50.44°, and 74.10°, which indicates that the active component studied in this work is copper (Cu). The dramatic increase in peak intensity may reflect the growth in crystal size and induce of active phase dispersion. It has been reported by van der Grift et al.30,31 After reduction, the characteristic structure of ZnO-SiO2 still remained in Cu2Zn2Si4, whereas CuO was water in interlayer. Profile of 3(b) indicates three major weight losses at around 50-80 °C, 80-150 °C and 150-300 °C. Temperature from 80-300 °C can be identified as external surfaces and H-bound water in Cu and Zn interlayer.29

Table 1. The structure of the calcined catalysts and Cu crystallite size in reduced catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Cu crystallite size (nm)</th>
<th>Pore volume (cm³/g)</th>
<th>Pore size (nm)</th>
<th>SBET (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu4Zn0Si4</td>
<td>23.7</td>
<td>0.377</td>
<td>3.59</td>
<td>282.29</td>
</tr>
<tr>
<td>Cu3Zn1Si4</td>
<td>20.8</td>
<td>0.313</td>
<td>3.75</td>
<td>140.62</td>
</tr>
<tr>
<td>Cu2Zn2Si4</td>
<td>15.4</td>
<td>0.252</td>
<td>4.10</td>
<td>96.66</td>
</tr>
<tr>
<td>Cu1Zn3Si4</td>
<td>27.4</td>
<td>0.274</td>
<td>3.43</td>
<td>91.61</td>
</tr>
</tbody>
</table>

*aCalculated based on desorption branch of isotherm.*
reduced. The XRD Peaks at $2\theta = 50.44^\circ$, and $74.10^\circ$ for Cu species were more visible when calcination temperature was increasing, which clearly shows that the crystal size of Cu increased with the increasing calcination temperatures. The crystallite size was calculated using Scherrer's equation: $D = \frac{0.9 \lambda}{\beta \cos \theta}$, where $\lambda$ is the x-ray wavelength (0.154 nm) and $\beta$ is the line broadening. The diameters of Cu crystals of reduced Cu2Zn2Si4 in temperature of 200 °C, 300 °C and 600 °C were calculated as 20 nm, 26 nm and 32 nm. In Figure 5, XRD patterns of catalysts with different Cu/Zn molar ratios were showed. These characteristic diffraction lines of cubic Cu crystals became prominent when without Zn additives, demonstrating that the Cu particles were small and well-dispersed at the loading of Zn. With the increasing loading of Zn, the crystallite size of Cu changed. The diameters of Cu crystals of reduced Cu4Zn0Si4, Cu3Zn1Si4, Cu2Zn1Si3, Cu2Zn2Si4, Cu1Zn2Si3 and Cu1Zn3Si4 at 200 °C were 31 nm, 30 nm, 22 nm, 20 nm, 24 nm and 27 nm. When Cu/Zn ratio was 1:1, the Cu particles were smallest. The results indicate that Cu species would be better stabilized and dispersed when Cu/Zn ratio was 1:1 in the silica support. Cu in Cu2Zn2Si4 catalyst that became representative crystal structure could be ascribed to partially loss of structure water in the gallery of catalysts during calcination, as shown in TGA.

**H2-TPR.** Figure 6 shows the H2-TPR profiles of calcined Cu4Zn0Si4 and Cu2Zn2Si4. Only one broader peak from 150 to 250 °C was detected in Cu2Zn2Si4. This hydrogen consumption could be designated to the reduction of Cu2+ ions existed on outside surface of lamellar and in lamellar structure of Cu2Zn2Si4. The reduction temperature is higher than that of Cu4Zn0Si4 that prepared without Zn, which indicated that Cu species in Cu2Zn2Si4 catalyst pre-treated with Zn loadings is more stable. The reduction of 0.25-CuZnAl catalyst with long tail (within 300 and 900 °C) is characteristic for the ZnO species on the solid surface. The XRD result in Figure 3 confirmed that characteristic structure in Cu4Zn0Si4 and Cu2Zn2Si4 remained after calcination and no separated ZnO could be detected. XRD results (Figures 4 and 5) show the presence of only metallic copper after the reduction of catalysts at 300 °C and it well conform to the TPR results. In this suggestion, homogeneously dispersed copper could be prepared via the reduced catalysts.

**Effect of Cu/Zn Molar Ratio on the Catalyst.** Cu-Zn/SiO2 catalysts with different compositions of Cu, Zn molar ratios were tested in the hydrogenation of EA. As shown in Figure 7, Cu/Si catalysts, Cu4Zn0Si4, represented the much lower conversions of 41.0%, respectively, while Cu-Zn/SiO2 catalysts showing conversions higher than 70%. This implies that the presence of ZnO in Cu based catalysts affects the activity of surface Cu, known as a catalytically active site for EA hydrogenation. It was additionally observed that the extents of rise in EA conversion depended on the Cu/Zn molar ratio. This finding was evidenced by the result that the catalysts with Cu/Zn molar ratio of 1:1 showed the extent of
rise in EA conversion. From the XRD result (Figure 5), catalyst with Cu/Zn ratio = 1:1 has the smallest Cu particles, so Cu species would be better stabilized and dispersed when Cu/Zn ratio was 1:1 in the silica support. Therefore, it is obvious that the Cu/Zn ratio plays a crucial role in the activity of Cu-Zn/SiO2 catalyst in the EA hydrogenation reaction, even though surface Cu is the active site.

Effects of Reaction Temperature on the Cu2Zn2Si4 Catalyst. Reactions were carried out at 150-300 °C (Figure 8). Temperature was critical in obtaining the desired ethanol selectivity. The conversion of EA increased from 1.2% to 79.0% upon increasing the reaction temperature from 150 °C to 250 °C and decreased to 71.2% when reaction temperature reached 300 °C. The hydrogenation of ethyl acetate was complicated by the subsequent formation of acetaldehyde. The reaction was found to be in equilibrium under the given reaction [Eq. (3)],

$$\text{C}_2\text{H}_5\text{OH} \leftrightarrow \text{CH}_3\text{CHO} + \text{H}_2$$

which had been discovered over silica-supported copper at temperatures near 570 K, however, it is reported that under conditions that the reaction temperature is lower than 670 °C, ethanol was the dominant product with some acetaldehyde and small amounts of CH₄ and CO being produced at high conversion.²⁷²⁸

EA hydrogenation is an exothermic reaction ($\Delta H = -28.5$ kJ/mol). According to Le Chatelier's principle, every system in stable chemical equilibrium submitted to the influence of an exterior force which tends to cause variation either in its temperature, in its totality or only in some of its parts, can undergo only those interior modifications change of temperature of a sign contrary to that resulting from the exterior force, which indicating that with the reaction temperature rose, thermodynamic equilibrium constant decreases which is benefit to reverse process, and it is not conducive to the generation of ethanol which was were well conformed to experiment result. Meanwhile, lower amounts of adsorbed reactants that have been found in other similar systems²⁷²⁸ may relate to chemical equilibrium since adsorption is also an exothermic phenomenon. It is clear that ethyl acetate is the thermodynamically favored product at low temperatures and that higher temperatures favor the ethanol, the reaction temperature is typically higher than 200 °C. However, reaction temperature higher than 300 °C may be further connected in series side effects, reducing the ethanol selectivity. It is apparent from the results that the desired product selectivity can be obtained by controlling the change of temperature.

Effects of Calcination Temperature on the Cu2Zn2Si4 Catalyst. Different calcination temperatures ranging from 120 °C to 600 °C (catalyst dried in air at 120 °C for 12 h, others calcined for 5 h) were tested on Cu2Zn2Si4. Under the different calcination temperatures, the EA hydrogenation activities were collected, as shown in Figure 9. It revealed that the optimal calcination temperature of the Cu2Zn2Si4 catalyst was 200 °C. As the calcination temperature increased from 200 °C to 600 °C, the EA conversion was gradually reduced.

Figure 8. Hydrogenation of EA over Cu2Zn2Si4, showing the effect of reaction temperature; catalysts calcination temperature = 200 °C, reduction temperature = 300 °C, H2 = 60 mL/min.

Figure 9. Hydrogenation of EA over Cu2Zn2Si4, showing the effect of catalysts calcination temperature; reduction temperature = 300 °C, reaction temperature = 250 °C, H2 = 60 mL/min, WHSV = 2 h⁻¹.

Figure 10. Hydrogenation of EA over Cu2Zn2Si4, showing the effect of catalysts reduction temperature; reaction temperature = 250 °C, calcination temperature = 200 °C, H2 = 60 mL/min, WHSV = 2 h⁻¹.
reduced while the selectivity to ethanol had no obvious change. As shown in XRD result (Figure 4), Cu in reduced Cu2Zn1Si1 catalyst which was calcined at 200 °C was well-dispersed, stable and had small particle size. These results indicated that the conversion of EA depends strongly on the particle size of copper, smaller sized copper is extremely active.

Effects of Reduction Temperature on the Cu2Zn1Si1 Catalyst. The effect of reduction temperature (without reduction) on the conversion of EA and selectivity to ethanol is shown in Figure 10 when the catalysts were reduced for 2 h in H2 flow at temperatures in the range from 200 to 400 °C. The conversion of EA was 57.0% and increased from 69.1% to 81.6% upon the increasing reduction temperature from 200 °C to 300 °C, while it decreased when the temperature was 400 °C. As shown in TPR, CuO was reduced within 100 and 250 °C, while ZnO reduced higher than 300 °C. It is apparent from the result that on the condition when CuO was completely reduced while ZnO keeping original formation was benefit to high EA hydrogenation conversion.

Conclusion

In summary, a highly active catalyst containing Cu, Zn and Si was synthesized for hydrogenation of ethyl acetate in this work, which was proved to be feasible in producing ethanol. This kind of copper catalyst exhibited predominant activity because of the homogeneously dispersion of copper species in the solid base. And this kind of solid base supported copper catalyst is also a material full of mesopores that enhanced the accessibility of reactants. A strong calcination and reduction temperature dependence of the as-prepared Cu-Zn/SiO2 catalyst was observed. The reduced catalyst with Cu/Zn ratio = 1:1 has the smallest Cu particles that would be better stabilized and dispersed. The Cu-Zn/SiO2 system calcined at 200 °C in the air and reduced at 300 °C with H2 achieved the most effective to activate H2 molecules, and in turn, gave the highest catalytic activities for EA hydrogenation. In a word, homogeneously dispersed copper on solid base could be synthesized by thermal decomposition of the precursors after coprecipitation method and this bimetallic catalyst is efficient and attractive for EA hydrogenation to ethanol.

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References