

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

Ying-ming Zhu and Xin Wang Li Shi*

The State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China

*E-mail: yyshi@ecust.edu.cn

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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·*n*H₂O 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 interest 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 process, such as acetaldehyde condensation or ethylene and acid addition now. Processes which include the hydrogenation of ethyl acetate have been proposed for the manufacture of basic chemicals (ethanol). Furthermore, there has been continuous interest over the past decades in replacing the existing, energy-intensive processes for the production of ethanol by more cost-effective routes involving ethyl acetate hydrogenation.

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, Folkers and Adkins¹⁷ first described the reaction that Catalytic hydrogenation of esters to two alcohols using copper-chromium catalyst [Eq. (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, Fe₂O₃ or ZnO²¹⁻²⁵ 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}



In our work, we studied the selective hydrogenation of EA to ethanol on Cu-Zn/SiO₂ 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 N₂-adsorption, X-ray diffraction (XRD), thermogravimetric (TG), temperature-programmed reduction with H₂ (H₂-TPR). Over the most-active catalyst, a systematic study of the hydrogenation reaction, including the influence of reduction temperature and reaction temperature, 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/SiO₂ Catalysts activity on ethyl acetate hydrogenation. From these results, an explanation was formulated for the catalysts structure and the role Zn on affecting the activity of Cu-Zn/SiO₂ catalysts.

Experimental

Catalyst Preparation. Hydrogenation components Cu-Zn/SiO₂ (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, Na₂SiO₃·9H₂O dissolved with stirring. To an aqueous solution containing appropriate amount of Cu(NO₃)₂·5H₂O, Zn(NO₃)₂·4H₂O (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 20 °C for 12 h. The filter cake was prepared *via* the kneading method. All the catalysts were carried out under atmospheric pressure at a temperature of 120 °C for 12 h. These materials are indicated in the following as Cu_xZn_ySi_{x+y} (x=4, y=0; x=3, y=1; x=2, y=1; x=2, y=2; x=1, y=2; x=1, y=3) while the Subscripts represent different Cu/Zn/Si molar ratios. Different calcination temperatures for the same time (5 h) in air were applied to the catalysts, in order to determine the influence of different calcination temperatures in EA hydrogenation. Before hydrogenation the catalysts were reduced under pressure at 1 MPa of different temperatures.

Characterization of Catalyst.

N₂-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 10⁻⁵ Torr to

a constant pressure. The isotherms could be used to calculate the specific surface area (S), micro pore volume (V_{mic}), total pore volume (V_t), average micro pore size (L_{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 Kα 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, 100mg catalysts of different calcination temperatures were prepared.

Temperature-Programmed Reduction: Temperature programmed reduction (TPR) of H₂ was carried out on Auto Chem 2910 (Micromeritics) instrument to study the reducibility of Cu-Zn/SiO₂ catalysts. In a typical experiment, 0.05 g of calcined catalyst was exposed to a reducing gas consisting of 5.0 vol % H₂ 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 unreduced catalyst (20-40 mesh) was loaded into the flow reactor. The catalyst was reduced in situ at atmospheric pressure with H₂ (flow rate of 30 cm³/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).

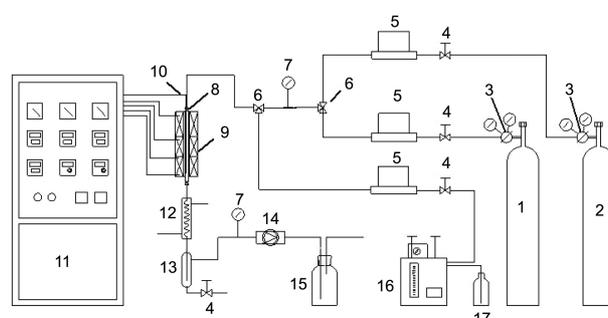


Figure 1. Fixed-bed Reaction System. 1-H₂; 2-N₂; 3-Reducing Valve; 4-Valve; 5-Mass Flow Meter; 6-Triple Valve; 7-Pressure Gauge; 8-Reactor; 9-Heater; 10-Thermocouple; 11-Temperature Controller; 12-Condenser; 13-Gas-Liquid Separator; 14-Back Pressure Valve; 15-Gas Washing Bottle; 16- Microsyringe Pump; 17-Raw Materials.

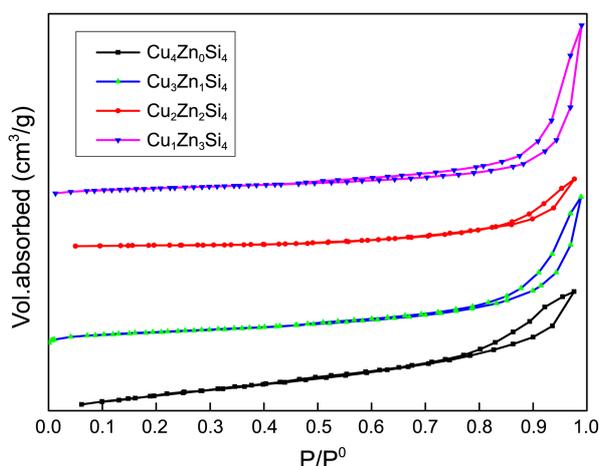


Figure 2. N₂-adsorption isotherms at -196 °C of Cu₄Zn₀Si₄, Cu₃Zn₁Si₄, Cu₂Zn₂Si₄ and Cu₁Zn₃Si₄.

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, Cu₂Zn₂Si₄ 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 hydroxalcite-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

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

Catalyst	Cu crystallite size (nm)	Structure		
		Pore volume ^a (cm ³ /g)	Pore size ^a (nm)	S _{BET} ^a (m ² /g)
Cu ₄ Zn ₀ Si ₄	23.7	0.377	3.59	282.29
Cu ₃ Zn ₁ Si ₄	20.8	0.313	3.75	140.62
Cu ₂ Zn ₂ Si ₄	15.4	0.252	4.10	96.66
Cu ₁ Zn ₃ Si ₄	27.4	0.274	3.43	91.61

^aCalculated based on desorption branch of isotherm.

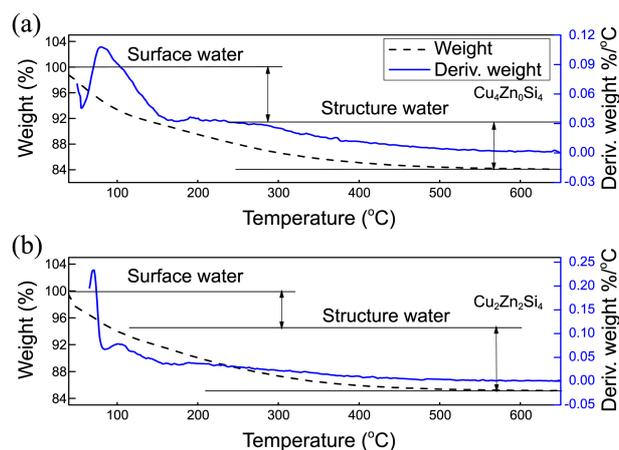


Figure 3. TGA curves of Cu₄Zn₀Si₄ and Cu₂Zn₂Si₄.

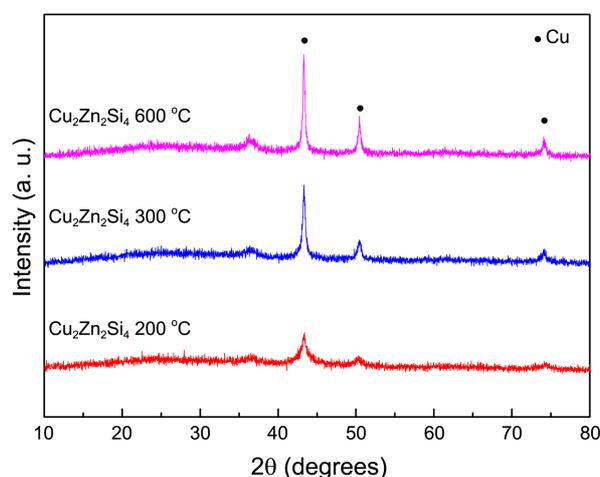


Figure 4. X-ray diffraction (XRD) pattern of reduced Cu₂Zn₂Si₄ (calcined in air of different temperatures for 5 h) samples. The catalysts were reduced under pressure at 1 MPa of 300 °C.

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 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

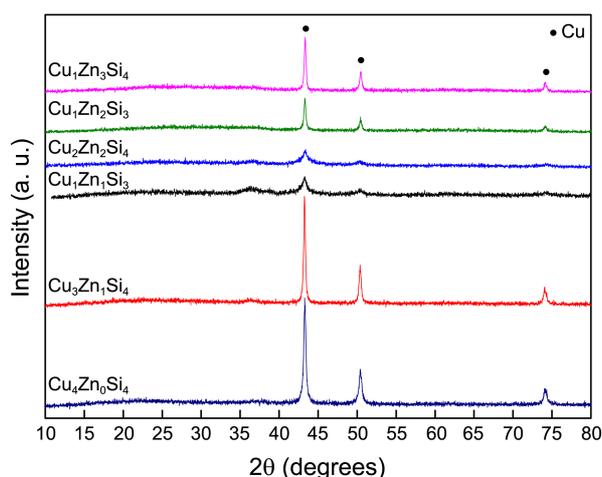


Figure 5. X-ray diffraction (XRD) pattern of reduced $\text{Cu}_4\text{Zn}_0\text{Si}_4$, $\text{Cu}_3\text{Zn}_1\text{Si}_4$, $\text{Cu}_2\text{Zn}_2\text{Si}_4$, $\text{Cu}_1\text{Zn}_3\text{Si}_4$ and $\text{Cu}_1\text{Zn}_3\text{Si}_4$ (calcined in air at 200 °C for 5 h). The catalysts were reduced under pressure at 1 MPa of 300 °C.

reduced. The XRD Peaks at $2\theta = 50.44^\circ$, and 74.10° 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.³² The crystallite size was calculated using Scherrer's equation: $D = 0.9 \lambda / (\beta \cos \theta)$, where λ is the x-ray wavelength (0.154 nm) and β is the line broadening. The diameters of Cu crystals of reduced $\text{Cu}_2\text{Zn}_2\text{Si}_4$ 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 $\text{Cu}_4\text{Zn}_0\text{Si}_4$, $\text{Cu}_3\text{Zn}_1\text{Si}_4$, $\text{Cu}_2\text{Zn}_2\text{Si}_4$, $\text{Cu}_1\text{Zn}_3\text{Si}_4$ and $\text{Cu}_1\text{Zn}_3\text{Si}_4$ 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 $\text{Cu}_2\text{Zn}_2\text{Si}_4$ 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 $\text{Cu}_4\text{Zn}_0\text{Si}_4$ and $\text{Cu}_2\text{Zn}_2\text{Si}_4$. Only one broader peak from 150 to 250 °C was detected in $\text{Cu}_2\text{Zn}_2\text{Si}_4$. This hydrogen consumption could be designated to the reduction of Cu^{2+} ions existed on outside surface of lamellar and in lamellar structure of $\text{Cu}_2\text{Zn}_2\text{Si}_4$.¹⁵ The reduction temperature is higher than that of $\text{Cu}_4\text{Zn}_0\text{Si}_4$ that prepared without Zn, which indicated that Cu species in $\text{Cu}_2\text{Zn}_2\text{Si}_4$ 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.³³ The XRD result in Figure 3 confirmed that characteristic struc-

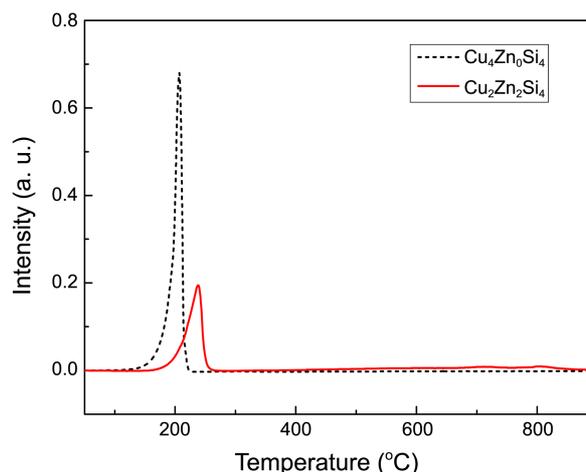


Figure 6. Temperature-programmed reduction (TPR) profiles of calcined $\text{Cu}_4\text{Zn}_0\text{Si}_4$ and $\text{Cu}_2\text{Zn}_2\text{Si}_4$ (calcined in air at 200 °C for 5 h) catalysts.

ture in $\text{Cu}_4\text{Zn}_0\text{Si}_4$ and $\text{Cu}_2\text{Zn}_2\text{Si}_4$ 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, $\text{Cu}_4\text{Zn}_0\text{Si}_4$, 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.^{19,27} 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

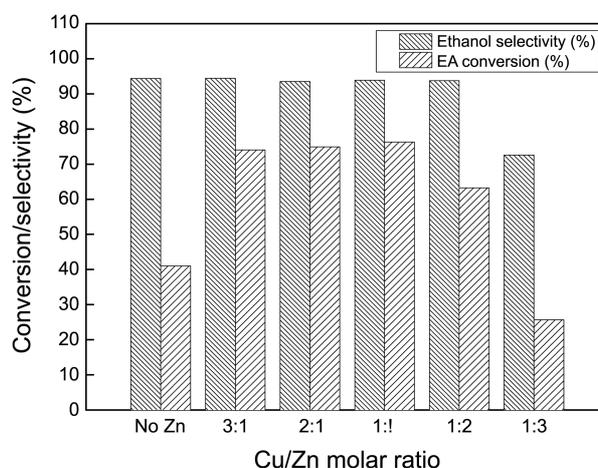


Figure 7. Hydrogenation of EA over Cu-Zn/SiO₂ catalysts of different Cu/Zn molar ratios; Conditions: catalysts calcination temperature = 300 °C, reduction temperature = 300 °C, reaction temperature = 250 °C, WHSV (weight hourly space velocity) = 2 h⁻¹ EA, H₂ flow = 60 mL/min.

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 acetate³⁴ was complicated by the subsequent formation of acetaldehyde. The reaction was found to be in equilibrium under the given reaction [Eq. (3)],



which had been discovered over silica-supported copper at temperatures near 570 K. however, it is reported that²⁷ 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.^{35,36}

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 systems^{37,38}

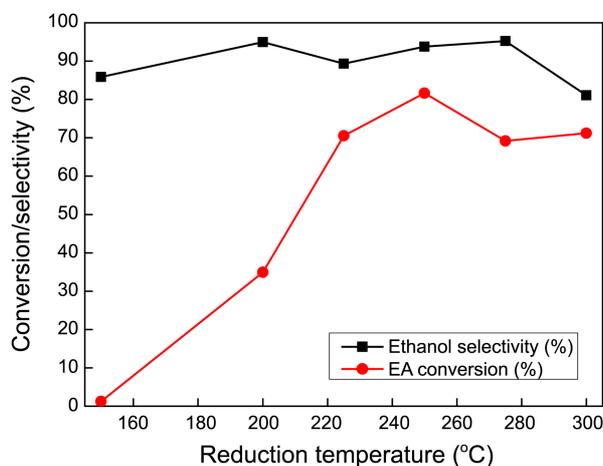


Figure 8. Hydrogenation of EA over Cu₂Zn₂Si₄, showing the effect of reaction temperature; catalysts calcination temperature = 200 °C, reduction temperature = 300 °C, H₂ = 60 mL/min.

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

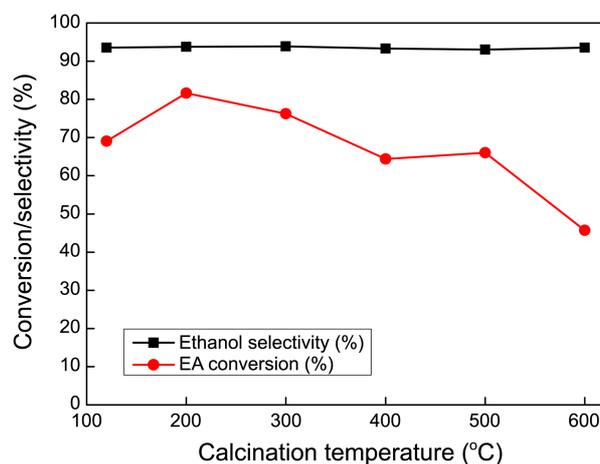


Figure 9. Hydrogenation of EA over Cu₂Zn₂Si₄, showing the effect of catalysts calcination temperature; reduction temperature = 300 °C, reaction temperature = 250 °C, H₂ = 60 mL/min, WHSV = 2 h⁻¹.

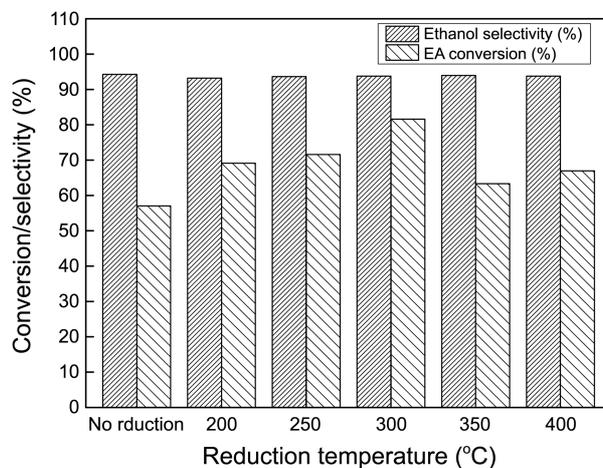


Figure 10. Hydrogenation of EA over Cu₂Zn₂Si₄, showing the effect of catalysts reduction temperature; reaction temperature = 250 °C, calcination temperature = 200 °C, H₂ = 60 mL/min, WHSV = 2 h⁻¹.

reduced while the selectivity to ethanol had no obvious change. As shown in XRD result (Figure 4), Cu in reduced $\text{Cu}_2\text{Zn}_2\text{Si}_4$ 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 $\text{Cu}_2\text{Zn}_2\text{Si}_4$ 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 H_2 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 H_2 achieved the most effective to activate H_2 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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