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A Highly Effective Cu/ZnO/Al_2O_3 Catalyst for Hydrogenation of Methyl Benzoate to Benzyl Alcohol in Methanol Solution

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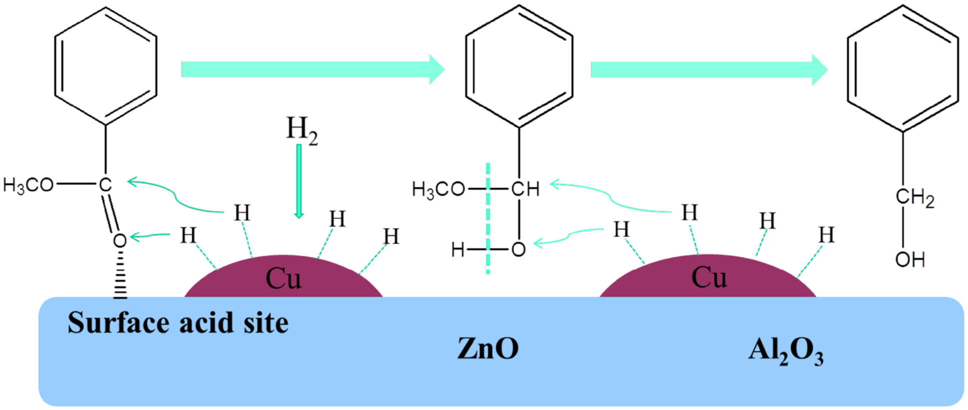
Abstract

The Cu/ZnO/Al_2O_3 catalysts prepared by co-precipitation method were used for the hydrogenation of methyl benzoate to benzyl alcohol. These catalysts were characterized at various stages of preparation by nitrogen adsorption–desorption, X-ray diffraction (XRD), hydrogen temperature-programmed reduction (H_2-TPR), and X-ray photoelectron spectroscopy (XPS). The experimental results show that the addition of ZnO to the catalyst greatly improves the selectivity of benzyl alcohol. When the Cu/Zn/Al molar ratio is 2:2:1 and the calcination temperature of the catalyst is 650 °C, the catalyst exhibits very highly catalytic performance. In addition, the effects of reaction temperature, pressure and time were also investigated during the hydrogenation of methyl benzoate to benzyl alcohol. When the methyl benzoate was hydrogenated over this catalyst at 160 °C and 7 MPa of H_2 for 10 h, the conversion of methyl benzoate can reach 93.89% and the selectivity of benzyl alcohol is 88%. This effectively catalytic performance can be attributed to the presence of highly dispersed and stable metallic copper nanoparticles, and the weak acidity of the catalyst surface. Besides, the reaction pressure and temperature play a crucial role in the conversion of methyl benzoate and the selectivity of benzyl alcohol.

Graphical Abstract

Application of Cu/ZnO/Al_2O_3 catalyst in hydrogenation of methyl benzoate to benzyl alcohol.



Keywords Cu/ZnO/Al_2O_3 catalysts · Liquid-phase hydrogenation · Methyl benzoate · Benzyl alcohol · Weak acidity

1 Introduction

Benzyl alcohol is an important chemical solvent for inks, paints, varnishes, and used as a precursor for various esters in the cosmetics and coatings industry [1]. As early at the 1940s, Adkins pioneered the development of a series of

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Cu/Cr/Ba oxide-containing catalysts for hydrogenation of lactate-hydrogenated α-amino and hydroxy esters and hydrogenation of methyl and butyl hexanoate for preparing the corresponding alcohols. Due to the inherent resistance of the ester, especially for the reduction reaction [2, 3], the current heterogeneous catalytic process is usually carried out under extremely harsh conditions. At the same time, Mozingo and Folkers [4] began to study the reaction of Cu/CrO_3/BaO catalysts for the hydrogenation of aromatic esters to prepare the corresponding alcohols in methanol. In the past decade, a series of strategies have been developed to prepare aromatic alcohols from corresponding esters. The inorganic metal hydride (such as $LiAlH_4$ and $NaBH_4$) was used as a catalyst to reduce the ester, but it suffered poor compatibility with functional groups, low atomic utilization, and wastes producing [2, 5]. The benzyl chloride hydrolysis method was also used to prepare benzyl alcohol. However, the inevitable introduction of free chloride ions cannot satisfy the high quality of benzyl alcohol which is applied in the food and pharmaceutical industries. Therefore, developing highly efficient and environmentally friendly catalysts is a long-term goal for researchers.

In general, catalysts for ester hydrogenation are prepared by mixing a hydrogenation metal (e.g., Fe, Co, Ni, Cu, Zn) with various oxides (e.g., ZrO_2, V_2O_5, Cr_2O_3, WO_3) [6]. Especially the copper-based catalysts exhibit excellent performance in the hydrogenation of esters to the corresponding alcohols [7–12]. Among them, Cu/ZnO/Al_2O_3 is widely used as a highly efficient and environmentally friendly catalyst due to their excellent activity and selectivity for the hydrogenation of C=O bands [13, 14]. The studies hold various views on the rule of ZnO in the reaction of ester hydrogenation to produce the corresponding alcohol, such as storing hydrogen, activating hydrogen [15–17], and also increasing the dispersion of Cu particles. However, to our knowledgement, no detailed and in-depth study of the effects of Cu-based catalysts has been reported in the hydrogenation of esters to produce the corresponding alcohols [18].

In view of cost and practical application, the hydrogenation of benzoate to benzyl alcohol is an essential industrial reaction and will be widely used in the industrial production of benzyl alcohol. Because benzoic acid methyl ester can be obtained by direct esterification with benzoic acid and methanol, the cost of the substrate and industrial production can be greatly reduced. Therefore, the hydrogenation of benzoic acid methyl ester to produce benzyl alcohol will be a great practical significance in industry.

In this work, The Cu/ZnO/Al_2O_3 catalyst synthesized by the co-precipitation method was first used in the hydrogenation of methyl benzoate to benzyl alcohol. Their physic-cochemical and catalytic properties for hydrogenation of methyl benzoate were investigated. We have found that highly dispersed Cu and weakly acidic sites play an important role in the hydrogenation of methyl benzoate to benzyl alcohol. Besides, the effect of reaction condition of catalysts on their catalytic performances were discussed. The Cu/ZnO/Al_2O_3 catalyst exhibits high catalytic activity and benzyl alcohol selectivity in this reaction, which may be applied to the hydrogenation of methyl benzoate to produce benzyl alcohol in industry.

2 Experimental

2.1 Catalyst Preparation

The precursor of Cu/ZnO/Al_2O_3 catalysts were synthesized by the co-precipitation method. $Cu(NO_3)_2 \cdot 3H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ (A.R., Sinopharm Chemical Reagent Ltd.) were used as the iron source and Na_2CO_3 was the precipitation. Typically, 1.0 M $Cu(NO_3)_2$, 1.0 M $Zn(NO_3)_2$, 1.0 M $Al(NO_3)_3$ and 0.5 M Na_2CO_3 were prepared respectively. The 1.0 M $Cu(NO_3)_2$ and 1.0 M $Zn(NO_3)_2$ solution was introduced into a precipitation vessel at 70 °C. At the time, an aqueous of Na_2CO_3 (0.5 M) was dripped into the vessel until the pH at 7.5 under constant stirring. Also, the $Al(NO_3)_3 \cdot 9H_2O$ was dripped by the same method described above. Then, the above two samples were mixed under the same condition. This synthesis solution was aged under constantly stirring for 2 h at 70 °C and cooled maintaining for 30 min. The precipitate was filtered and washed with deionized water until the filtrate appears to be neutral. Then the precursor material was dried at 100 °C for 12 h. The catalyst was obtained after heated to 450 °C at 5 °C min^{-1} and calcined at 450 °C for 4 h in a flow of air atmosphere.

2.2 Catalytic Reaction

The catalytic hydrogenation of benzoate to benzyl alcohol was performed in a 100 stainless steel under constant stirring at a speed of 500 rpm. Before testing the activity of the catalyst, the calcined CuO/ZnO/Al_2O_3 (1 g) sample was reduced in a 10% H_2/Ar atmosphere at 250 °C for 4 h at a heating rate of 5 °C min^{-1}. The autoclave was charged with 1 g of the freshly reduced catalyst, 0.5 g of methyl benzoate ($\geq$99.0%) and 25 mL of methanol solution. Then the autoclave was sealed, purging three times with hydrogen to replace the air. The autoclave was pressured at 3 MPa with hydrogen at room temperature, and the reaction temperature was maintained at 200 °C. Finally, reactants and products were analyzed by Shimadzu GC-14B gas chromatography equipped with flame ionization detector and Agilent DB-WAX capillary column.

2.3 Catalyst Characterization

The specific surface areas of the $Cu/ZnO/Al_2O_3$ catalysts were analyzed and measured by Nitrogen adsorption–desorption at − 196 °C on a Micromeritics ASAP 2020M analyzer, was calculated the porous volume and pore size using the Barrett–Joyner–Halenda (BJH) method.

The power X-ray diffraction (XRD) patterns of catalysts were collected on a Rigaku D max-2550 diffractometer with nickel-filtered Cu K radiation ($\lambda = 1.54$ Å).

The H_2-temperature-programmed reduction (H_2-TPR) was performed on a conventional flow system equipped with a thermal conductivity detector (TCD) as follow: sample was loaded in a quartz U-tube reaction, was treated at 120 °C for 1 h under flow of argon (30 mL min^{-1}). After it was cooled to 50 °C under flow Nitrogen, it was changed to 10% H_2/Ar (30 mL min^{-1}), and TPR of the catalyst was heated from 50 to 400 °C.

The NH_3-temperature-programmed desorption (NH_3-TPD) of the catalyst were carried out using a convention flow system which was connected with thermal conductivity detector (TCD). The calcined $CuO/ZnO/Al_2O_3$ sample (50 mg) was place in a quartz U-tube reaction that was pretreated at 450 °C for 30 min under a Nitrogen flow atmosphere (30 mL min^{-1}) at a rate of 10 °C min^{-1}. Then the sample was cooled to 100 °C at the same condition that followed by treatment with the 10% NH_3/N_2 (30 mL min^{-1}) for 30 min.

The X-ray photoelectron spectroscopy (XPS) was performed on a Thermo ESCALB 250 system with a Mg Kα source (1254.6 ev). The XPS spectra were calibrated by adjusting the position of the C 1 s peak to 284.6 eV.

The transmission electron microscope (TEM) observation were carried out on a TECNAI F20 electron microscope with on an operating voltage of 200 kV.

3 Results and Discussion

3.1 Textural and Structural Properties of Catalysts

The physicochemical and surface properties of CZA-X (X mean the different molar ratio of Cu, Zn and Al) catalysts calcined at 450 °C are shown in the Table 1. It can be clearly seen that with the addition of ZnO to Cu/Al_2O_3, the BET surface area of the CAZ-X-450 catalyst has dropped significantly from 61.2 to 40.4 $m^2\ g^{-1}$. However, the surface area of the catalysts also increases with the increase of the Zn contents. CZA-2-T catalysts (CZA-T, T mean the calcination temperature) exhibit decrease tendency of the area from 50.5 to 29.8 $m^2\ g^{-1}$ with the treatment temperature increasing (Table S1). Especially, CZA-2-750 sample shows the dramatically decreased surface area at 9.1 $m^2\ g^{-1}$, which indicates a significant sintering of the catalyst at high calcination temperature.

Table 1 Physisorption results of the $Cu/ZnO/Al_2O_3$ catalysts prepared by co-precipitation method at a series of different Cu/Zn/Al ratio

Samples	Molar ratio of Cu/Zn/Al	S_{BET} ($m^2\ g^{-1}$)	Pore volume[b] ($cm^3\ g^{-1}$)	Pore size[a] (nm)
CZA-0	2:0:1	61.2	0.071	3.88
CZA-1	2:1:1	40.4	0.056	5.81
CZA-2	2:2:1	37.1	0.075	6.99
CZA-3	2:3:1	51.0	0.120	8.47

[a] BJH desorption pore size

[b] BJH desorption average pore diameter

From the patterns of CZA-X-450 catalysts in Fig. 1a, it can be seen five obvious peaks at 35.52°, 35.45°, 35.55°, 38.73°, 38.92°, which are the characteristic peaks of CuO (JCPDS 05-0661). As shown in Fig. 1b, the XRD patterns of the reduced CZA-X-450 catalysts present clearly three strong diffraction peaks at 43.3°, 50.4° and 74.1°, which correspond to the (111), (200) and (116) planes of metallic copper phase (JCPD 65-9743). This indicates that the Cu^{2+} transferred to Cu^0 after the reduction process. In addition, the diffraction peaks at $2\theta = 31.77°$, 34.42° 36.25°, 47.54°, 56.60°, 62.86° and 67.96° can be found in the unreduced and reduced CZA-X-450 catalysts, which are characteristic peaks of ZnO (JCPDS 36-1451). Besides, no diffraction peaks of Al_2O_3 can be observed in the XRD patterns of all catalysts, which indicates that the Al_2O_3 were amorphous or highly dispersed in the unreduced and reduced CZA-X-450 catalysts. From the XRD results, we can found that the reduction treatment can change the valence state of Cu, while the Al and Zn states were unchanged.

The XRD patterns of CZA-2-T catalysts are shown in Fig. S1c. It is evident that CuO and ZnO diffraction peaks were observed in the patterns. The intensity of CuO and ZnO diffraction peaks gradually increase with the treatment temperature increasing. It may be caused by the Cu specific area loss of the CZA-2-T catalysts reduced [20]. At the same time, the XRD patterns of the reduced CZA-2-T catalysts were performed in Fig. S1d. No CuO diffraction peaks can be observed in the XRD patterns of all catalysts, which indicates that CuO has been completely reduced to metallic copper. With increasing the calcination temperature, the average crystallite size of metallic copper particles estimated by the Scherrer formula according to the (111) plane decreases gradually (Table S3). Besides, the XRD patterns of the used CZA-2-650 catalyst are shown in Fig. S3. It is clear that Cu and ZnO diffraction peaks remains unchanged.

The reducibility of the unreduced CZA-X-450 catalysts was measured by H_2-TPR (Fig. 2). It shows that reduction

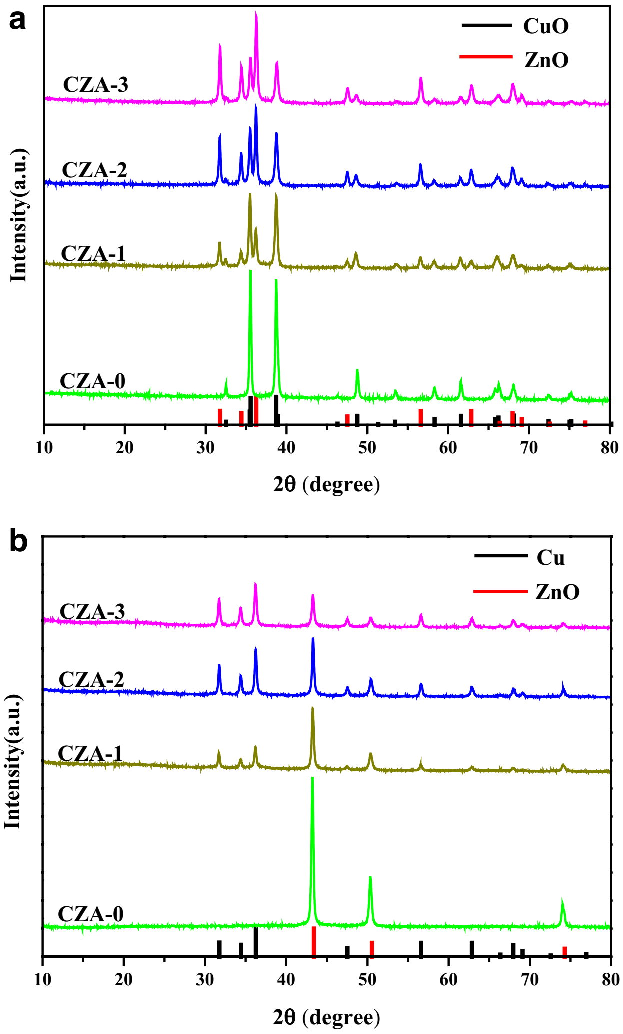


Fig. 1 XRD patterns of CZA-X-450 catalysts unreduced (**a**) and reduced (**b**)

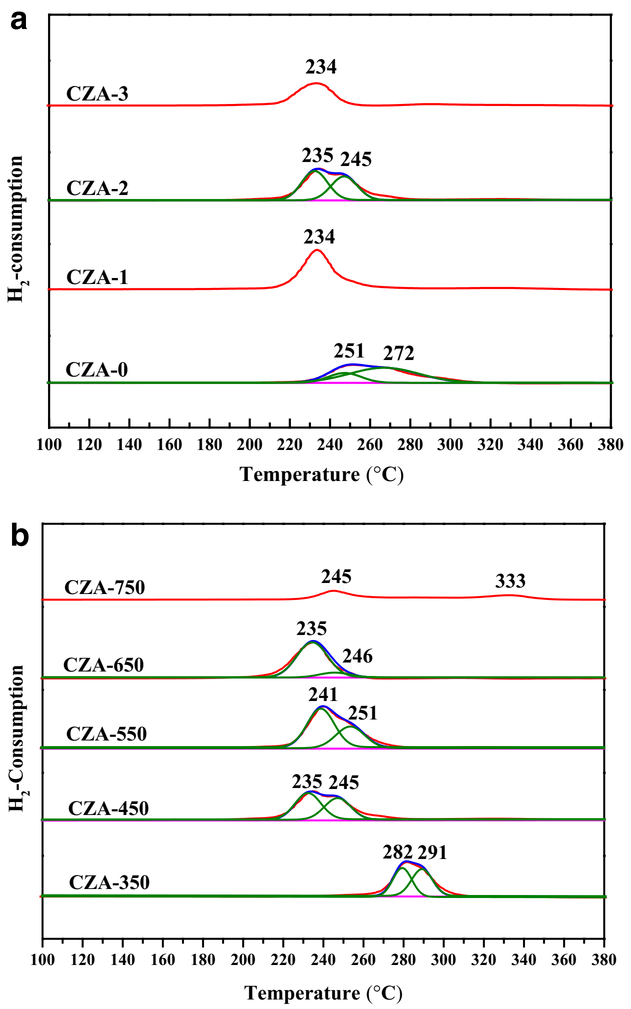


Fig. 2 H_2-TPR profiles of CZA-X-450 catalysts (**a**) and CZA-2-T catalysts (**b**)

peak of CZA-X-450 catalysts located at about 210–320 °C. Compared to unreduced CZA-0-450 catalyst, a much lower temperature (234 °C) peak was observed of CZA-1-450, CZA-2-450 and CZA-3-450 catalysts. In addition, two reduction peaks could be observed in the profiles of CZA-0-450 and CZA-2-450. The lower temperature peak can be attributed to the reduction of highly dispersed CuO particles and high temperature peak belongs to the reduction of bulk CuO particles [19, 20]. It is clearly shown that the reduction peak of the CZA-X-450 catalysts shift towards to the low temperature when ZnO is introduced into the catalyst. It is well-known that the presence of ZnO can promote the reduction of CuO by the hydrogen spillover [21, 22]. In addition, ZnO and Al_2O_3 cannot be reduced at below 500 °C [23, 24]. In the previous article [18], it was reported that the addition of ZnO to Cu/Al_2O_3 can form a Cu–Zn–O solid solution which can be reduced at a lower temperature compared to CuO. With the increasing of Zn/Al molar ratio, the reduction temperature of CZA-3-450 catalyst gradually shifts towards the low temperature, which indicates that CuO is highly dispersed in the catalyst.

In order to further investigate the reducibility of CZA-2-T catalysts treated at different temperature, the TPR characterization was performed as shown in the Fig. 2b. Two peaks can be observed in Fig. 2b. Copper species in CZA-2-T catalysts are reduced at different temperatures. The CZA-2-350 catalysts exhibits a higher reduction temperature in the range of 270–310 °C, which could be assigned to the reduction of bulk CuO particles [25]. With the calcination temperature increasing, the CZA-2-450 and CZA-2-650 catalysts exhibit lower reduction temperatures. Especially, the CZA-2-650 catalyst exhibits the lowest reduction temperature at 235 °C, with a smallest shoulder peak at 246 °C, suggesting that the electronic interaction exists in catalyst. This may change the electronic environment around CuO and make the CZA-2-650 catalyst more easily reduced [26]. In addition, it may be attributed to the presence of highly dispersed CuO nanoparticles, which could be easily reduced [7].

In the previous report, toluene and benzene were formed by catalytic hydrogenolysis of benzyl alcohol [8]. And acidic center of the catalyst surface affects the efficiency of C–O hydrogenolysis [27–29]. Therefore, NH$_3$-TPD was performed to evaluate the surface acidity of the CZA-X-450 catalysts. As shown in the Fig. 3a, four similar broad peaks can be observed obviously. It can be divided into two peaks (α and β). The α peak center is located at approximately 210–215 °C, which can be ascribed to weak acid sites. The β peak center is located at approximately 300–325 °C, which can be ascribed to medium acidic sites. The acidic sites of the CZA-X-450 catalyst are provided by ZnO, CuO, and Al$_2$O$_3$, but largely contributions are derived from the Al$_2$O$_3$ support [30]. With the Zn/Al molar ratio increasing, the intensities of the α and β peaks gradually decreased, which can be attributed to the reduction of the weaker and medium-strong acid site amount. The CZA-2-450 catalysts had the smallest amount of acid sites among the CZA-X-450. However, the catalyst acidity gradually increases as the ZnO content increase, which may be due to the increase in specific surface area of the catalyst [31].

The NH$_3$-TPD is also performed to evaluate the surface acidity of the CZA-2-T catalyst in the Fig. 3b. It is clearly seen that the CZA-2-350, CZA-2-450, CZA-2-550 and CZA-2-650 have a similar broad peak located at 150–430 °C. It can be also deconvoluted into two peaks (α and β). With the increase of calcination temperature at 350–650 °C, the CZA-2-650 had the smallest amount of acid sites, which may be due to decrease in the specific surface area of the catalyst [32]. As for CZA-2-750 catalyst, the peaks in the figure can hardly be observed. Considering the higher calcination temperature, the dramatic decrease should be correlated with the sintering of the catalyst, in which a large number of surface acidic sites have been lost [33, 34].

X-ray photoelectron spectroscopy (XPS) was employed to investigate the surface chemical states and compositions of the reduced Cu/ZnO/Al$_2$O$_3$ catalysts. As shown in Fig. 4, the peaks centered at 932.6 and 952.9 eV should be assigned to the binding energy of Cu 2p$_{3/2}$ and Cu 2p$_{1/2}$. Meanwhile, the absence of "shakeup" peaks of the binding energy (BE) at 940–945 eV may indicate that Cu^{2+} was completely reduced to metallic copper (Cu^0) and/or Cu$^+$ for the reduced Cu/ZnO/Al$_2$O$_3$ composites [35–38]. In addition, In addition, the atomic concentration of related elements is shown in Table S3.

Figure 5 shows the HRTEM images of reduced CZA-2-650 and ZCA-2-750 catalysts. It is apparent that the 15–17 nm copper nanoparticles are uniformly dispersed on the surface of the support and with a few agglomeration for

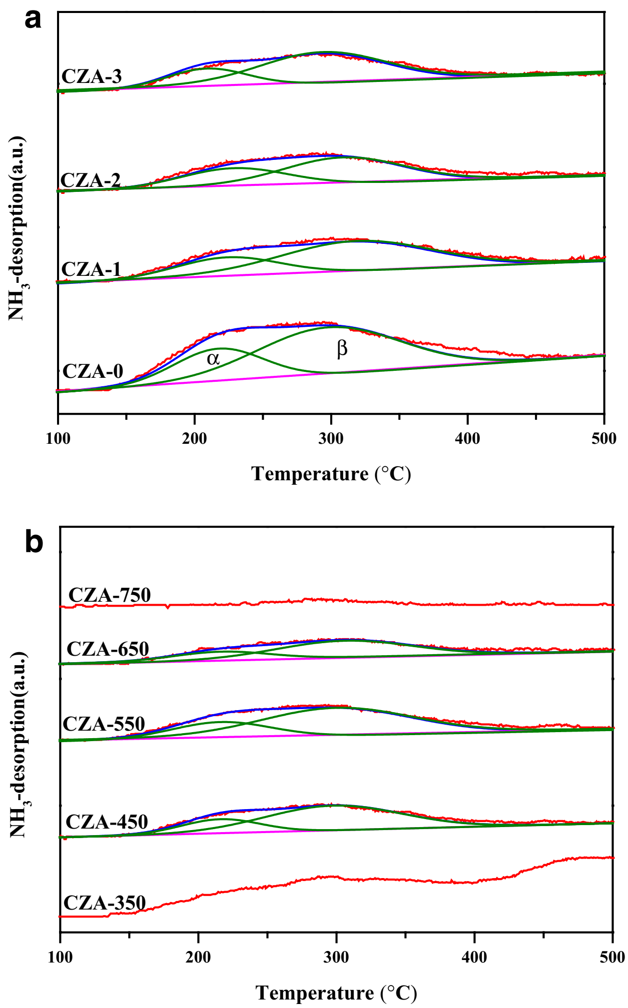


Fig. 3 NH$_3$-TPD profiles of CZA-X-450 catalysts (**a**) and CZA-X-T catalysts (**b**)

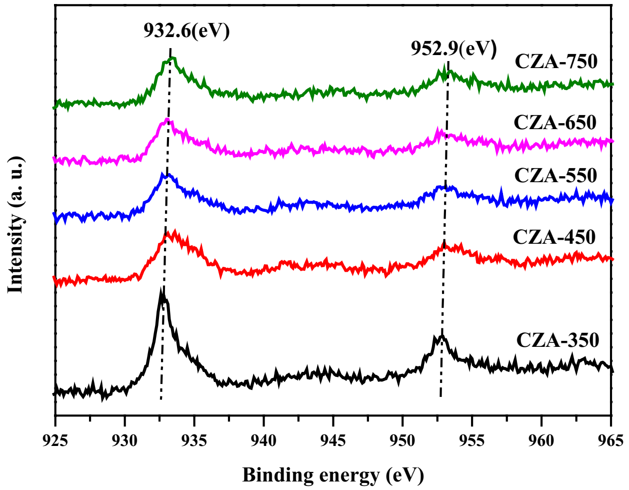


Fig. 4 The Cu^{2}p X-ray photoelectron spectra of reduced CZA-2-T catalysts

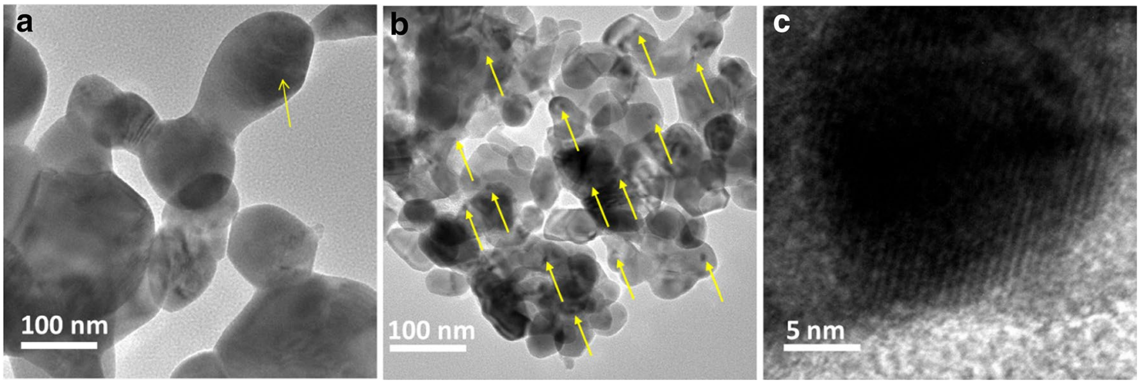


Fig. 5 TEM and HRTEM images of reduced CZA-2-650 and CZA-2-750 catalysts

Table 2 Effect of Zn/Al ratio on catalytic properties of Cu/ZnO/Al_2O_3 catalysts in the reaction of hydrogenation of methyl benzoate to benzyl alcohol

Catalysts	T (°C)	Time (h)	Conversion (%)	Selectivity (%)	
				BAOL	Toluene
CZA-0	200	8	73.13	24.40	75.60
CZA-1	200	8	51.21	81.94	18.06
CZA-2	200	8	62.45	81.00	19.00
CZA-3	200	8	32.17	84.12	15.88

Reaction conditions: methyl benzoate = 0.5 g; methanol = 25 mL, T = 200 °C; P = 3 MPa; n = 500 rpm (the speed is shown on the panel in the reactor of speed control); mCu/ZnO/Al_2O_3 = 1 g (catalysts calcined 4 h at 450 °C, reduced 4 h at 250 °C with 10% H_2/Ar)

the CZA-2-650 catalyst (Fig. 5b, c). As for the CZA-2-750 catalyst (Fig. 5a) some irregular large black copper particles, which should be mainly attributed to the sintering of copper particles.

3.2 Catalytic Performance of Cu/ZnO/Al_2O_3

Table 2 summarize the results of hydrogenation of methyl benzoate to benzyl alcohol over as-synthesized CZA-X-450 catalysts with different Cu/Zn/Al molar ratio, the yield of benzyl alcohol decreases in the following order for the catalysts: CZA-2-450 > CZA-1-450 > CZA-3-450 > CZA-0-450. It is clear that CZA-0-450 catalyst exhibits the lower yield of benzyl alcohol, while the selectivity of the corresponding toluene by-product was as high as 75.6%. This result indicates that the excessive acidity is more conducive to the hydrogenolysis of C–O to produce a large amount of by-product toluene in this reaction condition. However, with the addition of Zn, the selectivity of benzyl alcohol has been greatly improved. When the molar ratio of Zn/Al is 2, the conversion of methyl benzoate is 62.45%, and the selectivity of benzyl alcohol is 81%. This may be due to the fact that the addition of Zn reduces the surface acidity of the CZA-X-450 catalyst and increases the dispersion of Cu, inhibiting the formation of toluene by-products.

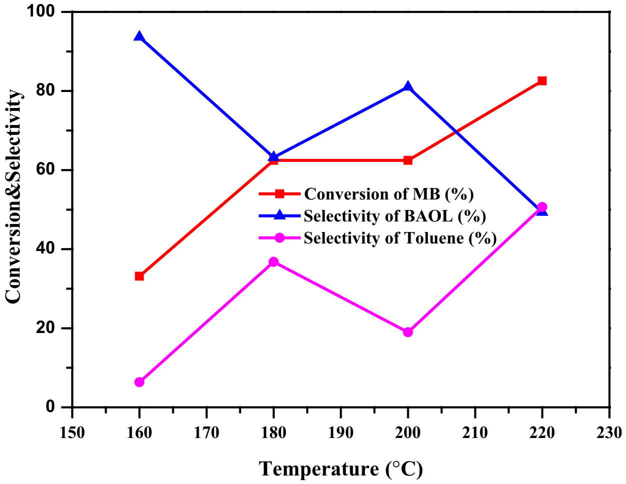


Fig. 6 Influence of reaction temperature on reaction of hydrogenation of methyl benzoate to benzyl alcohol

3.3 Effect of Reaction Conditions on the Hydrogenation of Methyl Benzoate

Based on the above results, the CZA-2-450 is an optimized catalyst for the hydrogenation of methyl benzoate to benzyl alcohol. Therefore, the CZA-2-450 catalyst was used to investigate the influence of the reaction conditions, including reaction pressure, temperature and time.

The effect of reaction temperature on the reaction is shown in the Fig. 6. The results show that the conversion rate of methyl benzoate is increased with the reaction temperature. When the temperature is 200 °C, the conversion rate of methyl benzoate and benzyl alcohol selectivity reaches a better value. Therefore, the appropriate reaction temperature is 200 °C. However, when the reaction temperature increases to 220 °C, the selectivity of benzyl alcohol drops rapidly.

That implies that the high temperature is not favorable for the selectivity of benzyl alcohol.

Figure 7 shows the effect of hydrogen pressure on this reaction. It is clearly seen that the conversion of methyl benzoate increases with improving hydrogen pressure. When the hydrogen pressure is 3 MPa, the conversion rate of benzoic acid methyl ester and benzyl alcohol selectivity reaches an optimal value. Therefore, when the reaction temperature is 200 °C, the appropriate reaction pressure is 3 MPa.

Effect of catalyst calcination temperature on the yield of benzyl alcohol was investigated at 350–750 °C, and the result was shown in the Table 3. The CA-2-650 catalyst exhibits the highest catalytic activity among the CA-2-T catalysts. At the same time, the H_2-TPR results show that the CZA-2-650 catalyst could be reduced at a lower temperature, which could be attributed to the presence of highly dispersed and easily reduced CuO nanoparticles [9]. Besides, the NH_3-TPD results suggest that the catalyst calcined at 650 °C has a weaker acidity. Therefore, it can be inferred that weaker acid sites is another important factor in increasing catalyst activity [29].

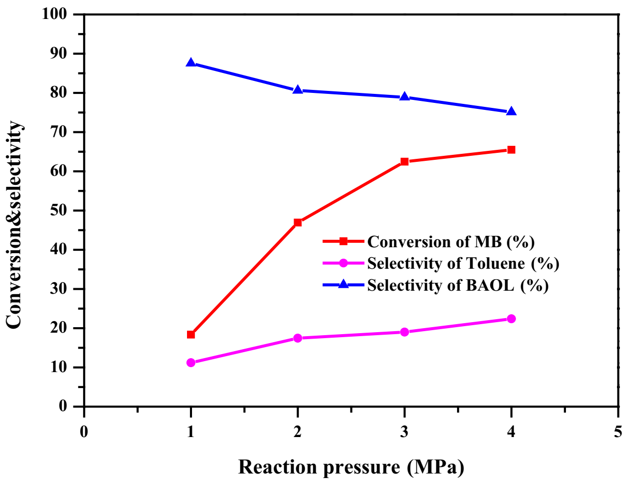


Fig. 7 Influence of reaction pressure on hydrogenation of methyl benzoate to benzyl alcohol

Table 3 Effect of Cu/ZnO/Al_2O_3 catalysts with different calcination temperatures on hydrogenation of methyl benzoate to benzyl alcohol

Catalysts	T (°C)	Time (h)	Conversion (%)	Selectivity (%)	
				BAOL	Toluene
CZA-2-350	200	5	48.61	85.93	14.07
CZA-2-450	200	5	49.39	90.11	9.89
CZA-2-550	200	5	44.85	86.23	13.77
CZA-2-650	200	5	70.85	72.00	28.00
CZA-2-750	200	5	25.84	88.83	11.17

Reaction conditions: methyl benzoate = 0.5 g; methanol = 25 mL, T = 200 °C; P = 3 MPa; n = 500 rpm (the speed is shown on the panel in the reactor of speed control); mCu/ZnO/Al_2O_3 = 1 g (catalysts calcined 4 h at 350 °C, 450 °C, 550 °C, 650 °C, 750 °C, reduced 4 h at 250 °C with 10% H_2/Ar)

3.4 Effect of Reaction Pressure and Temperature on Catalytic Efficiency of CZA-2-650 Catalyst

Under the above conditions, CZA-2-650 catalyst exhibits the highest catalytic activity. The conversion of methyl benzoate is up to 25.41% in the first hour (Fig. S2). However, the toluene by-product also increases rapidly with the increase of reaction time. It is obvious that further hydrogenation of benzyl alcohol could favorably occur under this reaction condition. Therefore, the condition of catalytic reaction should be continuously optimized based on the above results. Firstly, the effect of reaction temperature was investigated at 140–200 °C, and the reaction results are shown in Table 4. It is clear that the CZA-2-650 catalyst exhibits a better selectivity of benzyl alcohol (86%) at 160 °C, which can be served as the optimum reaction temperature. However, the conversion of methyl benzoate is lower in this reaction condition. In the previous article [4], the high pressure has a good catalytic efficiency in the hydrogenation of methyl benzoate to benzyl alcohol. Then, the effect of reaction pressure was investigated from 3 to 8 MPa (Table 5). It can be seen that the CZA-2-650 catalyst exhibits superior performance with increasing pressure. At a pressure of 7 Mpa, the conversion rate of methyl benzoate is 93.89%, and correspondingly selectivity of benzyl alcohol is 88%, which indicates that CZA-2-650 catalyst has excellent catalytic performance in this reaction condition (Scheme 1).

Based on the above experimental results, a possible reaction mechanism of hydrogenation of methyl benzoate could be concluded (Scheme 2). Firstly, Cu^0 should be an effective active center for the dissociation of H_2 in the hydrogenation of methyl benzoate. Then surface acid sites of catalysts can

Table 4 Effect of Cu/ZnO/Al_2O_3 catalysts with different reaction temperatures on hydrogenation of methyl benzoate to benzyl alcohol

Catalysts	T (°C)	Time (h)	Conversion (%)	Selectivity (%)	
				BAOL	Toluene
CZA-2-650	140	5	31.11	92.08	7.92
CZA-2-650	160	5	57.58	86.02	13.98
CZA-2-650	180	5	66.21	70.20	29.80
CZA-2-650	200	5	70.85	72.00	28.00

Reaction conditions: methyl benzoate = 0.5 g; methanol = 25 mL, T = 140–200 °C; P = 3 Mpa; n = 500 rpm (the speed is shown on the panel in the reactor of speed control); mCu/ZnO/Al_2O_3 = 1 g (catalysts calcined 4 h at 650 °C reduced 4 h at 250 °C with 10% H_2/Ar)

Table 5 Effect of $Cu/ZnO/Al_2O_3$ catalysts with different H_2 pressure on hydrogenation of methyl benzoate to benzyl alcohol

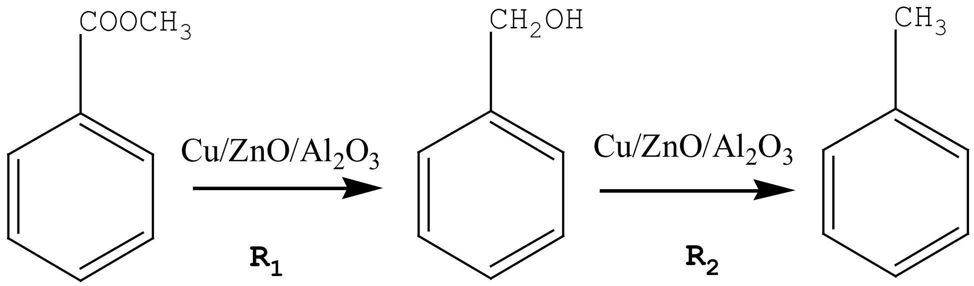
Catalysts	MPa	Time (h)	Conversion (%)	Selectivity (%)	
				BAOL	Toluene
CZA-2-650	3	10	80.67	68.78	31.22
CZA-2-650	4	10	82.01	80.58	19.42
CZA-2-650	5	10	90.68	83.56	16.44
CZA-2-650	6	10	94.85	76.92	23.08
CZA-2-650	7	10	93.89	88.00	12.00
CZA-2-650	8	10	86.94	93.26	6.74

Reaction conditions: methyl benzoate = 0.5 g; methanol = 25 mL, T = 160 °C; P = 3–8 Mpa; n = 500 rpm (the speed is shown on the panel in the reactor of speed control); $mCu/ZnO/Al_2O_3 = 1$ g (catalysts calcined 4 h at 650 °C reduced 4 h at 250 °C with 10% H_2/Ar)

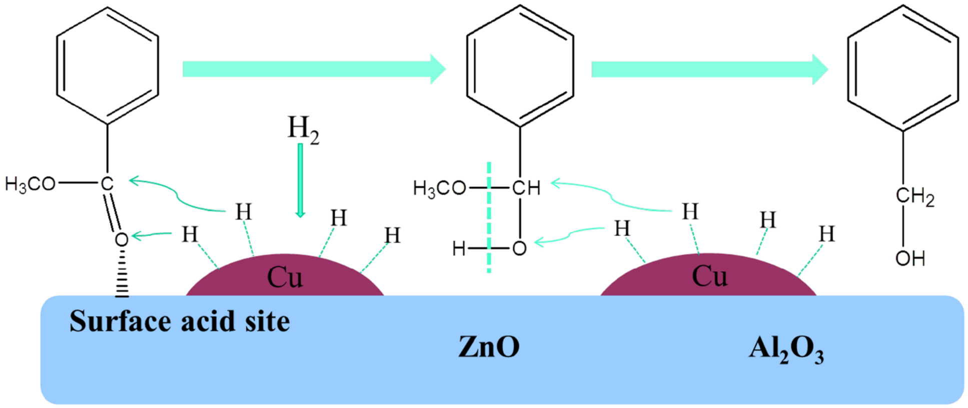
intimately absorb the reactant, which facilitates the activation of the reactant by virtue of the metallic Cu^0. Finally, it interact with the π* acceptor orbital of the C=O group, which facilities the nucleophilic attack of H to the carbon bearing a positive charge [39].

4 Conclusion

In summary, the preparation of $Cu/ZnO/Al_2O_3$ catalyst by co-precipitation method was used to investigate in the liquid-phase hydrogenation of methyl benzoate to benzyl alcohol. The CZA-2-650 catalysts exhibit the highest catalytic activity and selectivity. When the methyl benzoate was hydrogenated over this catalyst at 160 °C and 7 MPa of H_2 for 10 h, the conversion of methyl benzoate can reach 93.89%, and the selectivity of benzyl alcohol is 88%. The activity of $Cu/ZnO/Al_2O_3$ catalysts is not only related to highly dispersing copper nanoparticles, but also inextricably linked to the acidity of the catalysts and reaction temperature. Besides, we have found that higher reaction pressures effectively inhibit the hydrogenolysis of C–O. Therefore, the conversion of methyl benzoate and the selectivity of benzyl alcohol are greatly improved.



Scheme 1 Reaction pathway for the of methyl benzoate to benzyl alcohol



Scheme 2 Possible reaction mechanism of hydrogenation of methyl benzoate to benzyl alcohol catalyzed by $Cu/ZnO/Al_2O_3$

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