



Cite this: DOI: 10.1039/d0nj03201h

Effect of the ZnO/SiO₂ ratio on the structure and catalytic activity of Cu/SiO₂ and Cu/ZnO catalysts in water-containing ester hydrogenation†

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 Received 25th June 2020,
 Accepted 6th August 2020

DOI: 10.1039/d0nj03201h

rsc.li/njc

The effects of the ZnO/SiO₂ ratio on the water tolerance of Cu/SiO₂ and Cu/ZnO catalysts were studied by ethyl acetate with 5 wt% water hydrogenation. Notably, the addition of an appropriate amount of ZnO endows Cu/SiO₂ catalysts with satisfactory water-tolerant hydrogenation performance by a decrease in the reaction temperature without sacrificing conversion. At the same time, agglomeration can be alleviated for Cu/ZnO catalysts due to the optimal addition of SiO₂, which is considered as a partition material that effectively hinders the agglomeration of the Cu/ZnO catalyst. However, the addition of ZnO was not favourable for the copper dispersion of Cu/SiO₂. The stability of Cu/SiO₂ catalyst quickly degraded due to excessive ZnO being introduced by sintering. The copper dispersion of Cu/ZnO catalysts initially increased with increasing SiO₂ content, but then decreased. The addition of excess SiO₂ also led to decreased activity and rapid deactivation of the Cu/ZnO catalyst. In our study, the appropriate addition of ZnO (5 wt%) and SiO₂ (5 wt%) had a positive effect on the Cu/SiO₂ and Cu/ZnO catalysts, respectively.

1. Introduction

Copper is an inexpensive transition metal that has been widely used in different industries for reactions involving hydrogenation, adsorption, dyes, and others. In particular, copper can act as an active site for some hydrogenation reactions, for instance, methanol synthesis¹ and selective hydrogenation of various organic compounds,^{2–12} ascribed to its highly selective hydrogenation of C=O bonds and low activity for hydrogenolysis of the C–C bond.^{13,14} However, because metallic copper possesses a low $T_{\text{hüttig}}$ and T_{Tammann} , it is easy to grow at high reaction temperatures, which leads to the deactivation of copper-based catalysts.^{9,15} Fortunately, the use of supports with a large surface area can effectively promote the dispersion of metallic copper, as well as hinder the growth of metallic copper due to the strong interaction between copper and the supports.

SiO₂ has been widely used as a support for copper-based catalysts due to its inexpensive cost and strong interaction with

copper.^{9,16–18} Zhu and co-authors confirmed that the excellent stability (300 h) of glycerol hydrogenolysis was attributed to the strong interaction between Cu and SiO₂ species derived from chrysocolla.⁹ Tian *et al.* found that a greater amount of copper phyllosilicate could be obtained if the optimum calcination temperature was chosen.¹⁷ The large amount of copper phyllosilicate resulted in a high ratio of Cu⁺/Cu⁰, which was responsible for the hydrogenation performance. The published study also showed that the formation of copper phyllosilicate promoted the dispersion of copper species so that satisfactory catalytic activity was realized for methyl acetate hydrogenation.¹⁸ Therefore, the formation of copper phyllosilicate is beneficial for catalytic activity and stability of Cu/SiO₂ catalysts.

In our previous works, Cu/SiO₂ catalysts were chosen to study the effect of water on ethyl acetate hydrogenation due to its strong interaction between SiO₂ and copper.^{13,19} However, a high reaction temperature (280 °C) was required to obtain high catalytic activity. Furthermore, Fe, Co, Ni, and Zn were doped onto Cu/SiO₂ catalysts to improve the water-tolerant hydrogenation performance, and it was found that the Cu–Zn/SiO₂ catalyst showed the most optimal water-tolerant hydrogenation performance at a relatively low reaction temperature (240 °C).²⁰ Therefore, elemental Zn was responsible for the satisfactory water-tolerant hydrogenation performance of the Cu/SiO₂ catalyst.

ZnO is a support of copper-based catalysts that has also been extensively studied.^{21–26} Sehested *et al.* quantified zinc atoms in

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† Electronic supplementary information (ESI) available: Physicochemical property characterization of Cu/SiO₂ catalysts with different ZnO content and Cu/ZnO catalysts with different SiO₂ content are given in Table S1 and Fig. S1–S3. See DOI: 10.1039/d0nj03201h

a surface alloy of Cu/ZnO/Al₂O₃ catalyst to show the effect of ZnO as a promoter by a combination of chemisorption, reaction, and spectroscopic techniques.²¹ The Cu–ZnO catalyst produced by a coprecipitation method was used to explore the effect of solvent on the catalytic performance as Cu–ZnO participated in the hydrogenolysis of glycerol to 1,2-propanediol.²² The promotion effect of ZnO on copper-based catalysts in methanol synthesis was quantitatively analysed, and the results showed that strong interdependency existed between Zn coverage on a Cu surface and methanol synthesis activity.²³ Increased catalytic activity was observed when the hydrogenation of ethyl acetate to ethanol occurred, due to the addition of ZnO for Cu/ZnO/MO_x (MO_x = SiO₂, Al₂O₃ and ZrO₂) catalysts.²⁴ Huo and his team²⁵ used a ternary Cu/ZnO/Al₂O₃ catalyst to explore the catalytic transfer hydrogenation process of bio-based ethyl levulinate.

Core-shell CuZn_x@C materials exhibited more optimal catalytic activity than that of Cu@C for the hydrogenation of esters.²⁶ The reason for this phenomena was attributed to the simultaneous presence of Cu⁰ and Cu⁺ sites at ZnO crystal domains. Furthermore, the addition of a small amount of SiO₂ to Cu/ZnO catalyst greatly improved the catalyst stability by suppressing the crystallization of Cu and ZnO that would occur due to the production of water during methanol synthesis.²⁷ Therefore, the use of SiO₂ and ZnO played an important role in the catalytic performance of copper-based catalyst. Even so, to the best of our knowledge, the effect of the ZnO/SiO₂ ratio on the water-tolerant hydrogenation performance of Cu/SiO₂ and Cu/ZnO catalysts has not been systematically studied up to now.

In this work, Cu/SiO₂ catalysts with different ZnO content and Cu/ZnO catalysts with different SiO₂ content were prepared to explore the effect of the ZnO/SiO₂ ratio on the water-tolerant performance of Cu/SiO₂ and Cu/ZnO catalysts in an ethyl acetate hydrogenation reaction. Systematic characterizations were obtained to determine changes in the texture, composition, and structure of the catalysts. Additionally, the water-tolerant hydrogenation performances of the different Cu/SiO₂ and Cu/ZnO catalysts were correlated with the characterization results to reveal the reasons for the change in the water-tolerant

hydrogenation performance of catalysts due to the variations in the ZnO/SiO₂ ratio.

2. Experimental

2.1. Material

Copper(II) nitrate hydrate, zinc nitrate hexahydrate, ammonia solution (28 wt%) (Sinopharm Chemical Reagent Co., Ltd, AR) and Aerosil 200 (Degussa) were used as received. All reagents used in this work were of analytically pure grade and used without further purification.

2.2. Catalyst preparation

The ammonia evaporation-hydrothermal method was used to prepare Cu/SiO₂ catalysts. Specifically, copper nitrate trihydrate (6.05 g) and different amounts of zinc nitrate hexahydrate (ZnO/SiO₂ = 0, 5%, 10%, and 20%; wt%) were dissolved in deionized water (250 ml). After the copper nitrate trihydrate was completely dissolved, ammonia aqueous solution (30 g, 28 wt%) was added to form copper ammonia complex solution by peristaltic pump for 5 min. The solution was then maintained for 30 min at room temperature under vigorous stirring. After silica sol (14.76 g) was added, the solution was constantly stirred at 80 °C for 90 min. Subsequently, the mixture solution (80 ml) was poured into a 100 ml Teflon-lined autoclave and heated at 150 °C for 24 h. The obtained precipitates were washed several times with water and ethanol, and then centrifuged and dried at 80 °C for 4 h. On the basis of ZnO content, the prepared catalysts were marked as Cu/SiO₂, Cu/SiO₂-5Z, Cu/SiO₂-10Z, and Cu/SiO₂-20Z.

For Cu/ZnO catalysts, 6.05 g of Cu(NO₃)₂·3H₂O and 16.08 g of Zn(NO₃)₆·6H₂O were dissolved in 100 ml deionized water. Then, different amounts of Aerosil 200 (SiO₂/ZnO = 0, 5%, 10%, 15%, 95%; wt%) were added to the above-mentioned mixed solution under agitation. Subsequently, 200 ml NH₄HCO₃ aqueous solution was added under agitation, and the solution was maintained at 90 °C for 3 h under agitation, and then aged for 12 h. On the basis of SiO₂ content, the prepared catalysts were

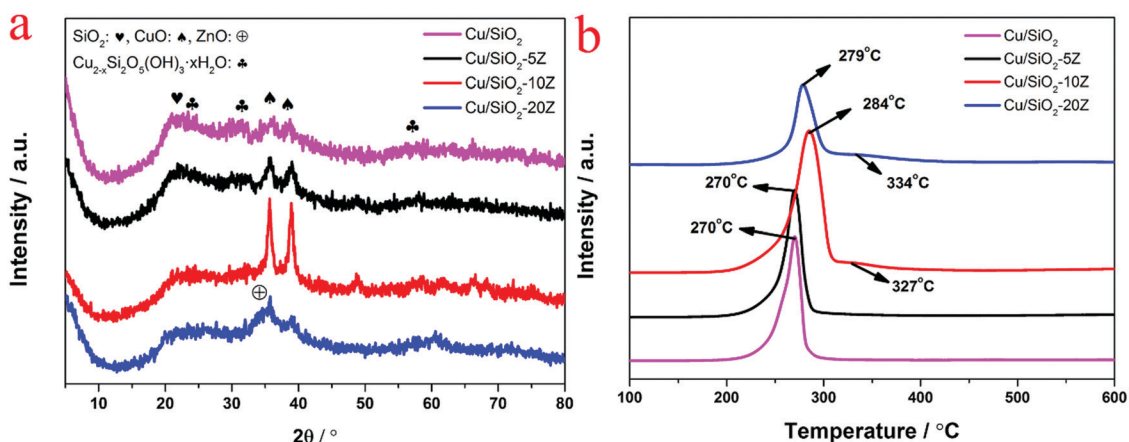


Fig. 1 (a) XRD pattern and (b) TPR of the Cu/SiO₂ catalysts with different ZnO content.

Table 1 The textural properties of Cu/SiO₂ catalysts with different ZnO content

Catalysts	S_{Cu} (m ² g ⁻¹)	D_{Cu} (%)	d_{Cu} (nm)
Cu/SiO ₂	247.6	36.6	2.7
Cu/SiO ₂ -5Z	214.7	31.7	3.2
Cu/SiO ₂ -10Z	168.1	24.9	4.0
Cu/SiO ₂ -20Z	85.6	12.7	7.9

$S_{Cu} = 1353 Y/X$, $D_{Cu} = 2 Y/X$, $d_{Cu} = 0.5 X/Y$. X = the area of the TPR1 peak and Y = the area of the TPR2 peak, which were determined by N₂O titration.^{25,26}

marked as Cu/ZnO, Cu/ZnO-5S, Cu/ZnO-10S, Cu/ZnO-15S, and Cu/ZnO-95S.

After that, the solutions were filtered and dried at 80 °C for 12 h. Then, the obtained precursors were calcined in a muffle furnace at 400 °C for 4 h. Finally, the obtained powders were pelletized, shed, and sieved to 40–60 mesh.

Additional information regarding the characterization and hydrogenation reaction conditions for all catalysts can be found in the ESI.†

3. Results and discussion

3.1. Physicochemical properties of the Cu/SiO₂ catalysts

The X-ray diffraction analysis was performed for Cu/SiO₂ catalysts with different ZnO content (Fig. 1a). From Fig. 1a, it was found that all catalysts contained silica (PDF #75-1555), chrysocolla (PDF #027-0188), and cupric oxide (PDF #45-0937).^{20,28} Specifically, the characteristic peaks of ZnO were not observed for the Cu/SiO₂-5Z and Cu/SiO₂-10Z catalysts, indicating that ZnO was uniformly distributed on the SiO₂ supports, while they could be observed for the Cu/SiO₂-20Z catalyst. In order to confirm the doping of ZnO, scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) of the Cu/SiO₂-5Z, Cu/SiO₂-10Z, and Cu/SiO₂-20Z catalysts was performed, and the results are summarized in Fig. S1 and Table S1 (ESI†). It was found that the copper loading decreased for the Cu/SiO₂-20Z catalyst, suggesting that the addition of excessive ZnO had a great effect on copper loading, while others exhibited content similar to that of the theoretical value (25 wt%).

Temperature-programmed reduction was carried out for the prepared catalysts using H₂, and the results are shown in Fig. 1b. From Fig. 1b, the peak area of hydrogen consumption of Cu/SiO₂-20Z was smaller than that of others, indicating that the content of copper oxides was lower. This phenomena was in agreement with the result obtained by SEM-EDS. This probably occurred because excessive ZnO had been used as a support, which led to the decreased of copper loading. Furthermore, a main and nearly symmetrical reduction peak could be observed, belonging to the reduction of copper species.^{9,29} At the same time, it was observed that the reduction temperature of copper species increased from 270 to 284 °C due to the addition of ZnO. This probably occurred because the interaction effect between Cu and SiO₂ was enhanced due to the addition of ZnO. The increase in copper particles with the

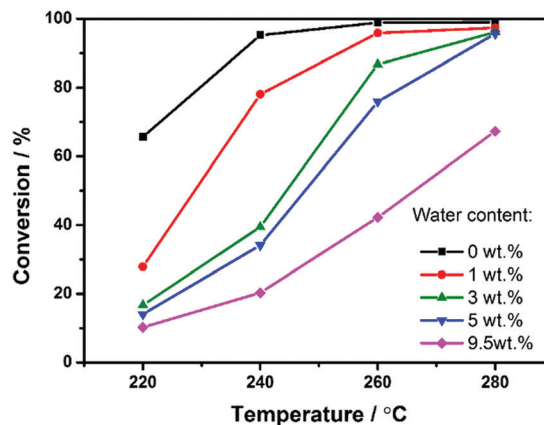


Fig. 2 The effect of water content on the hydrogenation performance of Cu/SiO₂ catalyst with increasing reaction temperature. Reaction conditions: $P = 2.5$ MPa, $n(H_2)/n(AcOEt) = 40$ (molar ratio), LHSV of AcOEt = $1 h^{-1}$, and the AcOEt contained 0, 1, 3, 5, and 9.5 wt% water.

increase in ZnO content may also be a reason, and this can be confirmed by the existence of the shoulder at 327 and 334 °C assigned to the reduction of large copper species particles for Cu/SiO₂-10Z and Cu/SiO₂-20Z catalysts.

N₂O titrations were performed to measure the dispersion (D_{Cu}), specific surface area (S_{Cu}), and average volume-surface diameter of metallic copper (d_{Cu}) (Table 1), and the corresponding curves are shown in Fig. S2 (ESI†). Table 1 shows that the d_{Cu} increased with the increase in ZnO content. Specifically, the d_{Cu} values for Cu/SiO₂, Cu/SiO₂-5Z, Cu/SiO₂-10Z, and Cu/SiO₂-20Z catalysts were 2.7, 3.2, 4.0, and 7.9 nm, respectively, which led to the decrease in D_{Cu} and S_{Cu} . Therefore, it was deduced that the addition of ZnO negatively affected the copper dispersion and easily caused the growth of catalyst particles after reduction, and this result was also confirmed by TEM.

3.2. Hydrogenation performance of the Cu/SiO₂ catalysts

The effect of the water content on hydrogenation performance of Cu/SiO₂ catalysts was studied by hydrogenation of ethyl acetate with 0, 1, 3, 5, and 9.5 wt% water, and the results are shown in Fig. 2. The hydrogenation performance of the Cu/SiO₂ catalysts decreased with increasing water content. The high reaction temperature (280 °C) also could not remedy the negative effect of the high water content (9.5 wt%) on conversion. In our study, the main product was ethanol, and the byproduct was ethane, and there was only a slight effect of the water content on the selectivity of ethanol, which had been confirmed by a previous study.¹⁹ On the basis of the above results, the water content of 5 wt% was chosen to study the effect of the ZnO/SiO₂ ratio on the Cu/SiO₂ and Cu/ZnO catalysts for hydrogenation of ester with water.

The water-tolerant hydrogenation performances of Cu/SiO₂ catalysts with different ZnO content were evaluated by ethyl acetate with 5 wt% water hydrogenation reaction (Fig. 3) at reaction temperatures from 200 °C to 260 °C. It was found that the ZnO content had a significant effect on the hydrogenation performance of AcOEt. Fig. 3a shows the change in hydrogenation

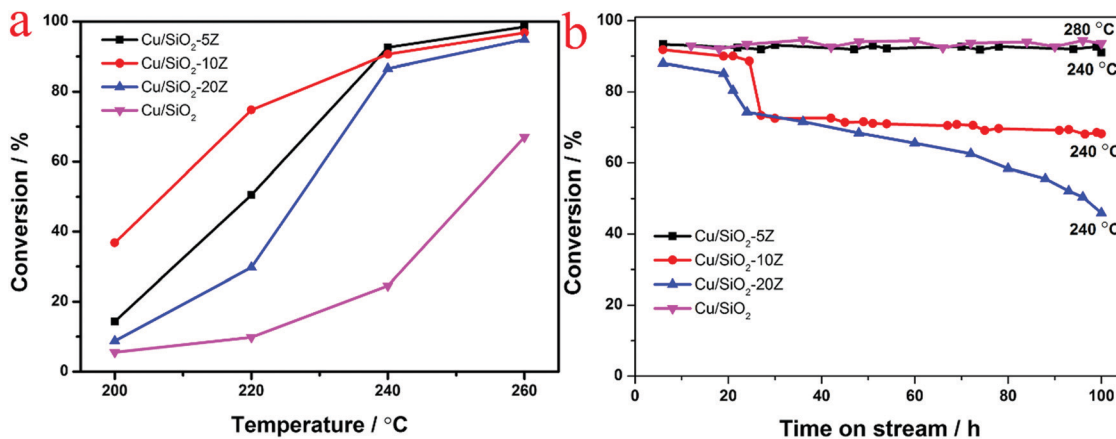


Fig. 3 (a) The change in hydrogenation performance with increasing reaction temperature and (b) the stability experiment for the catalysts with different ZnO content. Reaction condition: $P = 2.5$ MPa, $n(\text{H}_2)/n(\text{AcOEt}) = 40$ (molar ratio), LHSV of AcOEt = 1 h^{-1} , and the AcOEt contained 5 wt% water.

performance at different reaction temperatures. The conversion of AcOEt was increased with increasing reaction temperature, while ethanol selectivity decreased (Fig. S3, ESI[†]). Furthermore, the conversion was higher for Cu/SiO₂ catalysts with different ZnO content than that of the Cu/SiO₂ catalyst. The Cu/SiO₂-10Z catalyst exhibited more optimal catalytic performance at reaction temperatures below 240 °C, but the catalytic performance of the Cu/SiO₂-5Z catalyst exceeded that of the Cu/SiO₂-10Z catalyst at reaction temperatures greater than 220 °C.

In order to further study the effect of the ZnO content on the Cu/SiO₂ catalyst in the hydrogenation reaction, stability experiments were carried out at 240 °C for Cu/SiO₂-5Z, Cu/SiO₂-10Z, and Cu/SiO₂-20Z, and at 280 °C for the Cu/SiO₂ catalyst (Fig. 3b). Fig. 3b shows that the stability decreased with increasing ZnO content. Although the Cu/SiO₂ catalyst had the most optimal stability with high conversion (93%) as compared to others, it required a high reaction temperature

(280 °C). For the Cu/SiO₂-10Z and Cu/SiO₂-20Z catalysts, conversion of 90% can be obtained at the beginning of the reaction, but the conversion decreased with the time on stream. Especially, conversion of the Cu/SiO₂-10Z and Cu/SiO₂-20Z catalysts rapidly decreased at 20 h and then proceeded to slowly decrease. This probably occurred because the increase in the ZnO content facilitated the growth of copper species, and was confirmed by TEM (Fig. 4). However, there was no obvious deactivation observed for the Cu/SiO₂-5Z catalyst, and it maintained a high conversion (92%) at a reaction temperature of 240 °C. Therefore, the addition of a proper amount of ZnO, such as that for the Cu/SiO₂-5Z catalyst, can effectively decrease the reaction temperature without sacrificing the stability of the reaction.

The morphology of the fresh and spent catalysts was observed by TEM, as shown in Fig. 4. The addition of a small quantity of ZnO had little effect on particle size, but the effect was enhanced with increasing ZnO content. For the Cu/SiO₂

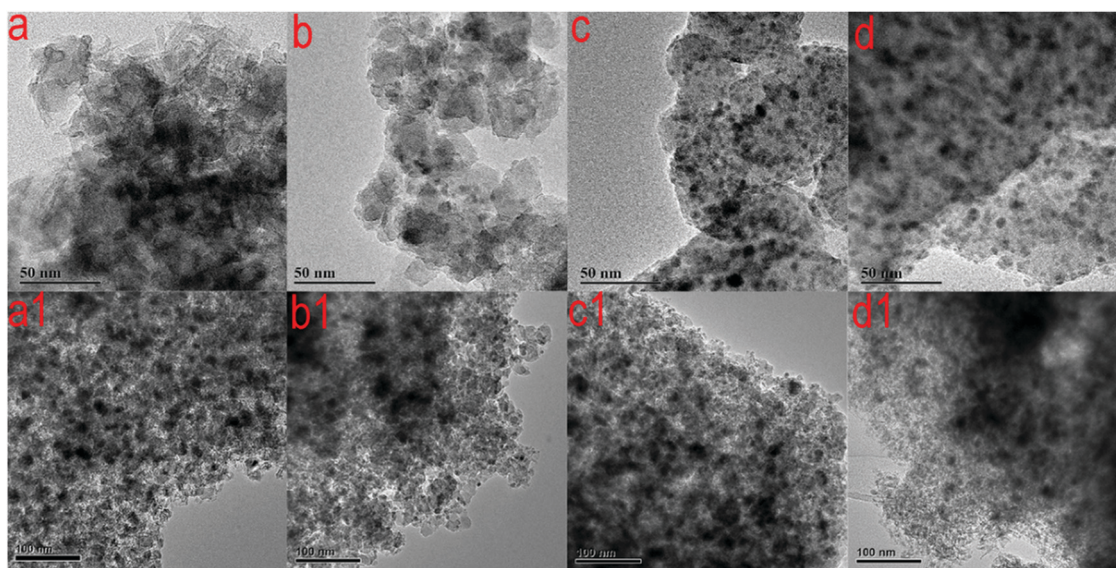


Fig. 4 TEM images of the (a) and (a1) Cu/SiO₂, (b) and (b1) Cu/SiO₂-5Z, (c) and (c1) Cu/SiO₂-10Z, and (d) and (d1) Cu/SiO₂-20Z catalysts before and after reaction.

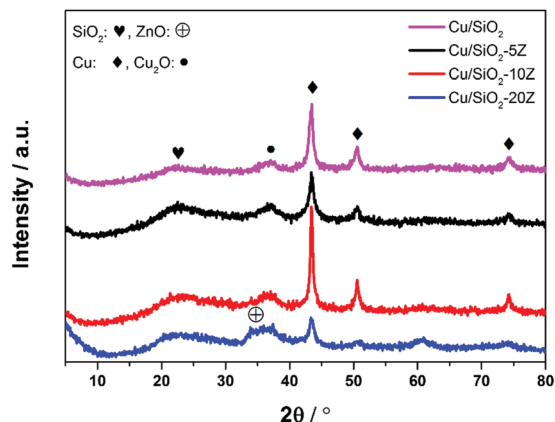


Fig. 5 XRD pattern of Cu/SiO₂ catalysts with different ZnO content after reaction.

and Cu/SiO₂-5Z catalysts, no obvious particles were observed (Fig. 4a and b), suggesting that copper species were evenly distributed on the SiO₂ supports. However, as ZnO increased, the copper species particle can be observed to grow, as shown in Fig. 4c and d, suggesting that the increasing ZnO content promoted the growth of copper species. Furthermore, the morphology of the catalysts after reaction is shown in Fig. 4a1–d1. It was found that the particle size of copper grew after reaction, and the sintering phenomenon can be observed from Fig. 4d1. This phenomena suggested that the catalysts were easy to sinter with increased ZnO content.

The XRD patterns of Cu/SiO₂ catalysts with different ZnO content after reaction are shown in Fig. 5. The strong peaks at 43.3°, 50.4°, and 74.1° were assigned to the characteristics of metallic copper (PDF #04-0836). Additionally, a small peak at 37.0° corresponded to the characteristics of Cu₂O (PDF #05-0667).¹³ Furthermore, no obvious characteristic peak of CuO was found, suggesting that the addition of ZnO did not cause severe oxidation of metallic copper. The characteristic peak of ZnO can only be observed for the Cu/SiO₂-20Z catalyst with a high ZnO content, as shown in Fig. 5.

As a result, the addition of ZnO had an important effect on the water-tolerant hydrogenation performance of the Cu/SiO₂

catalyst. The addition of the proper amount of ZnO can decrease the reaction temperature from 280 °C to 240 °C without sacrificing the conversion, selectivity, or stability of the reaction. In order to further confirm the effect of the ZnO/SiO₂ ratio on the water-tolerant performance of copper-based catalysts, Cu/ZnO catalysts with different SiO₂ content were prepared and evaluated.

3.3. Physicochemical properties of the Cu/ZnO catalysts

For Cu/ZnO catalysts with different SiO₂ content, XRD was also used to analyze their phase and structure, as shown in Fig. 6a. It was found that the characteristic peak intensity of ZnO (PDF #36-1451) decreased with increasing SiO₂ content, which indicated that the crystallinity of ZnO decreased. Specifically, the addition of a small amount of SiO₂ had little effect on the Cu/ZnO catalyst (for example, Cu/ZnO-5S), suggesting that SiO₂ was uniformly distributed on the ZnO supports. However, the greater the amount of SiO₂, the greater the effect on the Cu/ZnO catalyst. Similarly, temperature-programmed reduction (TPR) was also implemented for the Cu/ZnO catalysts (Fig. 6b). Fig. 6b shows that all reduction peaks had a shoulder before the main reduction peak. This probably occurred because the particle sizes of all Cu/ZnO catalysts were large, and thus, the surface copper species were initially reduced to form a shoulder peak, and then, the inner compositions were reduced. Simultaneously, the reduction temperature of copper species was almost unchanged (at approximately 270 °C) when the SiO₂ content was below 15 wt%. However, the reduction temperature decreased to 253 and 263 °C with the further increase in the SiO₂ content, suggesting that the copper ions were easily reduced. In other words, the addition of a large amount of SiO₂ weakened the interaction effect between Cu and ZnO. Furthermore, there was a dramatic decrease in the peak strength of hydrogen consumption with a SiO₂ content of 10 wt%, suggesting that SiO₂ had been used as a support rather than a dopant due to the addition of large amounts of SiO₂.

The dispersion (D_{Cu}), specific surface area (S_{Cu}), and average volume–surface diameter of metal copper (d_{Cu}) for Cu/ZnO catalysts were measured by N₂O titration, as shown in Table 2. The corresponding curves are also shown in Fig. S2 (ESI[†]). Obviously,

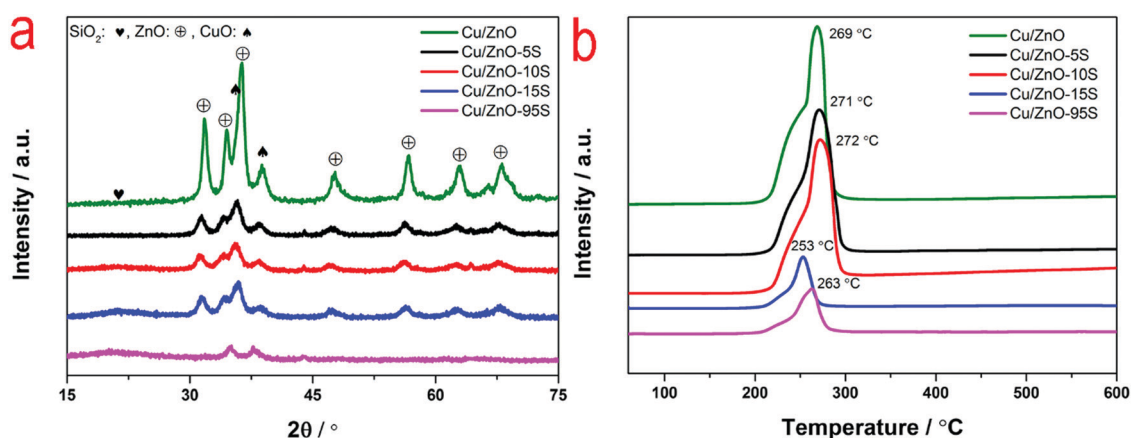


Fig. 6 (a) XRD pattern and (b) TPR of Cu/ZnO catalysts with different SiO₂ content.

Table 2 Textural properties of Cu/ZnO catalysts with different SiO₂ content

Catalysts	S_{Cu} (m ² g ⁻¹)	D_{Cu} (%)	d_{Cu} (nm)
Cu/ZnO	171.7	25.4	3.9
Cu/ZnO-5S	195.8	28.9	3.5
Cu/ZnO-10S	216.8	32.0	3.1
Cu/ZnO-15S	185.8	27.5	3.6
Cu/ZnO-95S	166.7	24.6	4.1

$S_{\text{Cu}} = 1353 Y/X$, $D_{\text{Cu}} = 2 Y/X$, and $d_{\text{Cu}} = 0.5 X/Y$. X = the area of the TPR1 peak and Y = the area of the TPR2 peak, which were determined by N₂O titration.^{25,26}

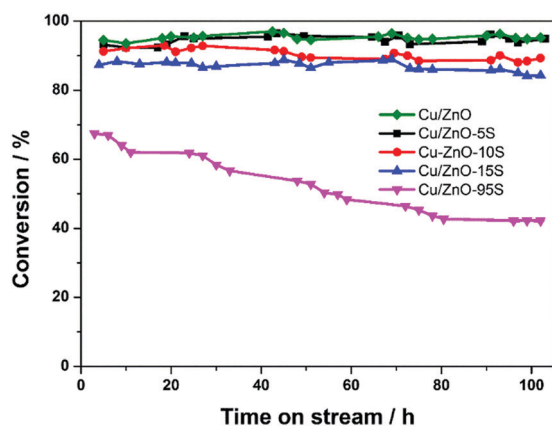


Fig. 7 The hydrogenation performance of Cu/ZnO catalysts with different SiO₂ content. Reaction conditions: $T = 240$ °C, $P = 2.5$ MPa, $n(\text{H}_2)/n(\text{AcOEt}) = 40$ (molar ratio), LHSV of AcOEt = 1 h^{-1} , and the AcOEt contained 5 wt% water.

the S_{Cu} and D_{Cu} of the Cu/ZnO catalysts increased when the SiO₂ content increased from 0 wt% to 10 wt% (Table 2). However, any further increase in the SiO₂ content will cause a decrease in S_{Cu}

and D_{Cu} . Specifically, the S_{Cu} increased from $171.7 \text{ m}^2 \text{ g}^{-1}$ to $216.8 \text{ m}^2 \text{ g}^{-1}$ and then decreased to $166.7 \text{ m}^2 \text{ g}^{-1}$ with increasing SiO₂ content (Table 2). This phenomena indicated that the addition of small amounts of SiO₂ (SiO₂ content < 10 wt%) was conducive to the dispersion of metallic copper. However, the addition of excess amounts of SiO₂ (SiO₂ content > 15 wt%) played a negative role in the dispersion.

3.4. Hydrogenation performance of the Cu/ZnO catalysts

Furthermore, the effect of the SiO₂ content on the Cu/ZnO catalyst in the hydrogenation reaction was studied by performing stability experiments, and the results are shown in Fig. 7. From Fig. 7, the Cu/ZnO catalyst exhibited satisfactory stability with high ethyl acetate conversion (95%), and no deactivation phenomena was observed within 100 h. The stability and conversion of the Cu/ZnO-5S catalyst were similar to that of the Cu/ZnO catalyst, suggesting that the addition of a small amount of SiO₂ had no effect on the stability and conversion. However, the stability and conversion was decreased with the further increase in the SiO₂ content. Specifically, the conversion had a small decline with the increased SiO₂ content, for example, the Cu/ZnO-10S and Cu/ZnO-15S catalysts, and slowly decreased with time on stream. Nevertheless, there was an obvious decrease in the conversion and stability for the Cu/ZnO-95S catalyst, suggesting that the addition of excess amounts of SiO₂ was unfavorable. This probably occurred because the addition of excess SiO₂ produced similar impacts on Cu/SiO₂ due to the addition of excess ZnO, which promoted the growth of copper species in the reaction.

For the Cu/ZnO, Cu/ZnO-5S, and Cu/ZnO-95S catalysts, TEM was used to monitor the morphology of the catalysts before and after the reaction (Fig. 8). Fig. 8a shows that the morphology of

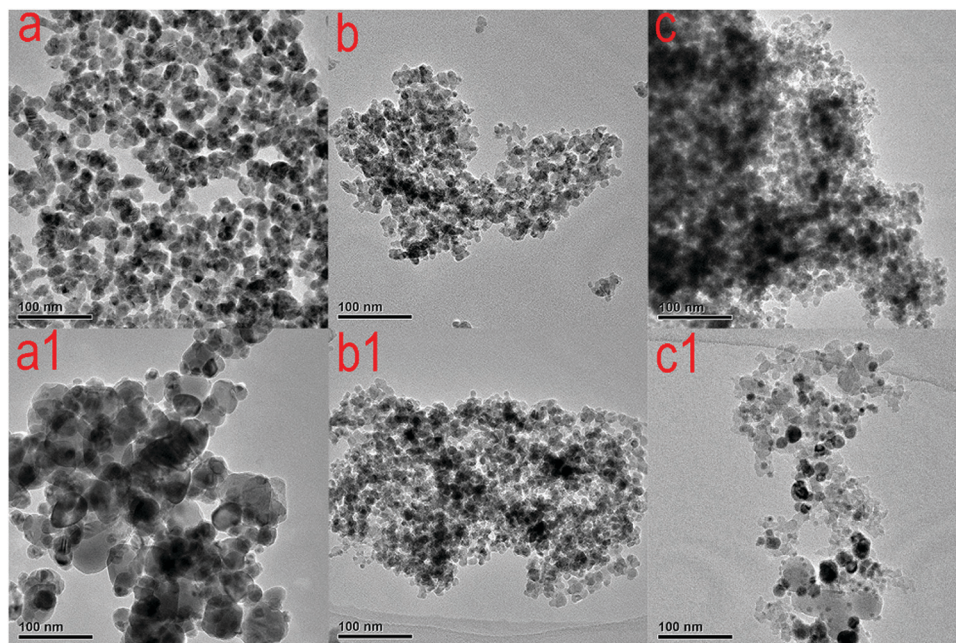


Fig. 8 TEM images of the (a) and (a1) Cu/ZnO, (b) and (b1) Cu/ZnO-5S, and (c) and (c1) Cu/ZnO-95S catalysts before and after reaction.

the Cu/ZnO catalyst was obviously different from the morphology of the Cu/SiO₂ catalyst (Fig. 4a). The morphology of the Cu/ZnO catalyst was spindle-shaped, while the morphology of Cu/SiO₂ was flake-like. With increasing SiO₂ content, agglomeration was clearly observed (e.g., Cu/ZnO-95S (Fig. 8c)), confirming that the addition of excess SiO₂ was not conducive to the dispersion of copper. At the same time, it was found that the particle of the Cu/ZnO catalyst significantly grew after the reaction (Fig. 8a1). However, an apparent reunion was not observed for the Cu/ZnO-5S catalyst after reaction (Fig. 8b1), suggesting that the addition of a small quantity of SiO₂ played a role in hindering catalyst agglomeration. In other words, a small amount of silica can act as a partitioning material to hinder the agglomeration of Cu/ZnO catalyst particles. Nevertheless, this effect was wakened with increasing SiO₂ content, for example, the Cu/ZnO-95S catalyst (Fig. 8c1). This may have occurred because there are similar impacts on Cu/SiO₂ due to the addition of excess ZnO that was produced with the increase in SiO₂ content. That is, if the Cu/ZnO catalyst was added to excess SiO₂, it can also be seen as the Cu/SiO₂ catalyst doping ZnO.

4. Conclusion

In this study, the effect of the ZnO/SiO₂ ratio on the water-tolerant hydrogenation of Cu/SiO₂ and Cu/ZnO catalysts was explored by ethyl acetate hydrogenation under reaction conditions with impure water. For the Cu/SiO₂ catalyst, the proper addition of ZnO can decrease the reaction temperature without sacrificing conversion, but the stability rapidly decreases as the ZnO content increases. This occurred because the catalyst particles were easy to sinter in the reaction due to the addition of ZnO. For the Cu/ZnO catalyst, which had 95% conversion of hydrogenation at relatively low reaction temperature, obvious agglomeration was found after the reaction. The addition of a small amount of silica (5 wt%) onto the Cu/ZnO catalyst acted as a partition, and it effectively hindered the agglomeration of Cu/ZnO catalyst particles. However, the addition of excess SiO₂ resulted in the Cu/ZnO catalyst producing effects similar to those that were caused by the addition of excess ZnO for the Cu/SiO₂ catalyst. Therefore, the appropriate addition of ZnO had a positive effect on the Cu/SiO₂ catalyst. Similarly, the positive effect can also be observed for the Cu/ZnO catalyst due to the appropriate addition of SiO₂.

Conflicts of interest

The authors declare no competing financial interests.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant No. 21673272, No. 21603257, and No. 21503256), the Chinese Academy of Sciences Strategic Pilot Science and Technology Special (Class A) (XDA21020000), and the autonomous research project of the State Key Laboratory of Coal Conversion (SKLCC 2018BWZ001).

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