

Understanding of the Key Factors Determining the Activity and Selectivity of CuZn Catalysts in Hydrogenolysis of Alkyl Esters to Alcohols

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Abstract: CuZn catalysts are perspective catalysts for esters hydrogenolysis, but more knowledge is needed to optimize their catalytic performance. In this work, we consider the impact of CuZn catalysts composition on their structure, activity, selectivity, and stability in esters hydrogenolysis. Four catalysts with various Cu/Zn ratio were synthesized by a co-precipitation and characterized in as-prepared, calcined, reduced, and spent state by XRF, XRD, N₂ physisorption, CO₂-TPD, NH₃-TPD, and N₂O chemisorption. XRD data revealed the effect of the composition on the size of Cu and ZnO particles. The catalytic performance was investigated using an autoclave. All catalysts exhibited high methyl hexanoate conversion about 48–60% after 3 h but their activity and selectivity were found to be dependent on Cu/Zn ratio. The conversion of methyl hexanoate and hexyl hexanoate was compared to explain the observed product selectivity. Moreover, the catalysts stability was investigated in three consecutive reaction cycles and correlated with changes in the size of constituent particles. Moreover, when different esters were tested, a slight decrease in conversion and increase in alcohol selectivity with a growth in molecule size was observed. Obtained results allow making a conclusion about the optimal composition that provides the good performance of CuZn catalysts in ester hydrogenolysis.

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1. Experiments on the evaluation of H₂ consumption during the reduction of CuZn-C samples varied by Cu/Zn ratio.

The curves of H₂ consumption during the reduction of CuO species in CuZn mixed oxides with different Cu/Zn ratio (Figure S1) evidenced that, regardless of the chemical composition of the samples, the reduction of constituent CuO species started at about 150 °C. The total amount of consumed H₂ increased with the growth of Cu content in the samples, and the obtained values on the H₂ consumption further allowed evaluating accessible copper particles.

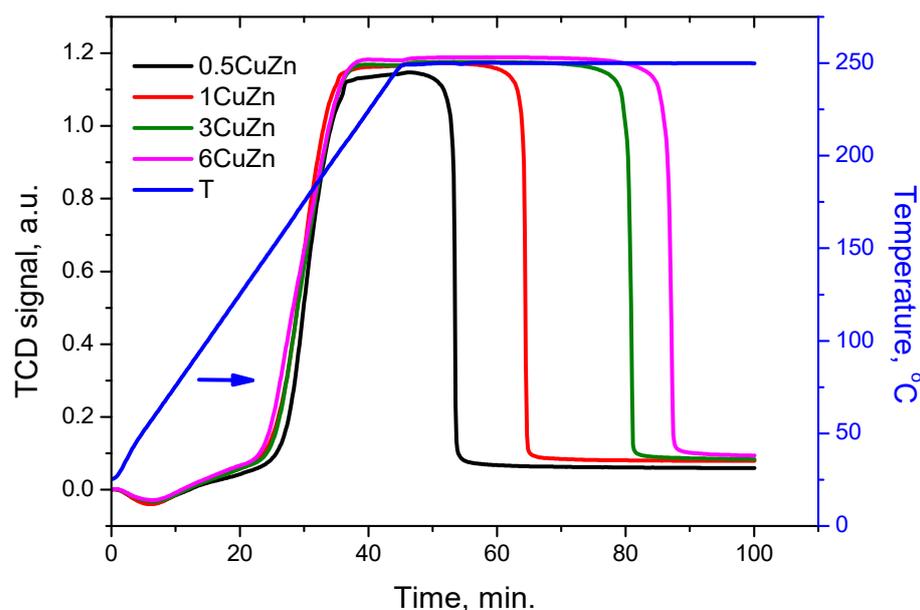


Figure S1. The profiles of H₂ consumption obtained for CuZn mixed oxides with different Cu/Zn ratio.

2. Results on the hydrogenolysis of MeHe+1-Heol mixture in presence of catalysts with different Cu/Zn ratio.

To get more understanding on the transesterification ability of CuZn-R catalysts, additional experiments on the hydrogenolysis of MeHe+1-Heol mixture in presence of the reduced samples with different Cu/Zn ratio. All experiments on the conversion of MeHe+1-Heol mixture (MeHe/1-Heol=2 mol) were performed at reaction conditions used for the hydrogenolysis of either MeHe or HeHe, i.e. T=210 °C and p=100 bar H₂. MeHe conversion was calculated based on the molar content of MeHe at the beginning of a catalytic run and at time *t*. The yield of transesterification products was calculated based on the molar fraction of MeHe converted to HeHe (Yield Trans), while the yield of hydrogenolysis products (Yield Hydro) was evaluated as a difference between total converted MeHe moles and MeHe moles converted to HeHe. The performance of pure CuO (Cu after reduction step) and ZnO taken as reference samples was also evaluated in the reaction.

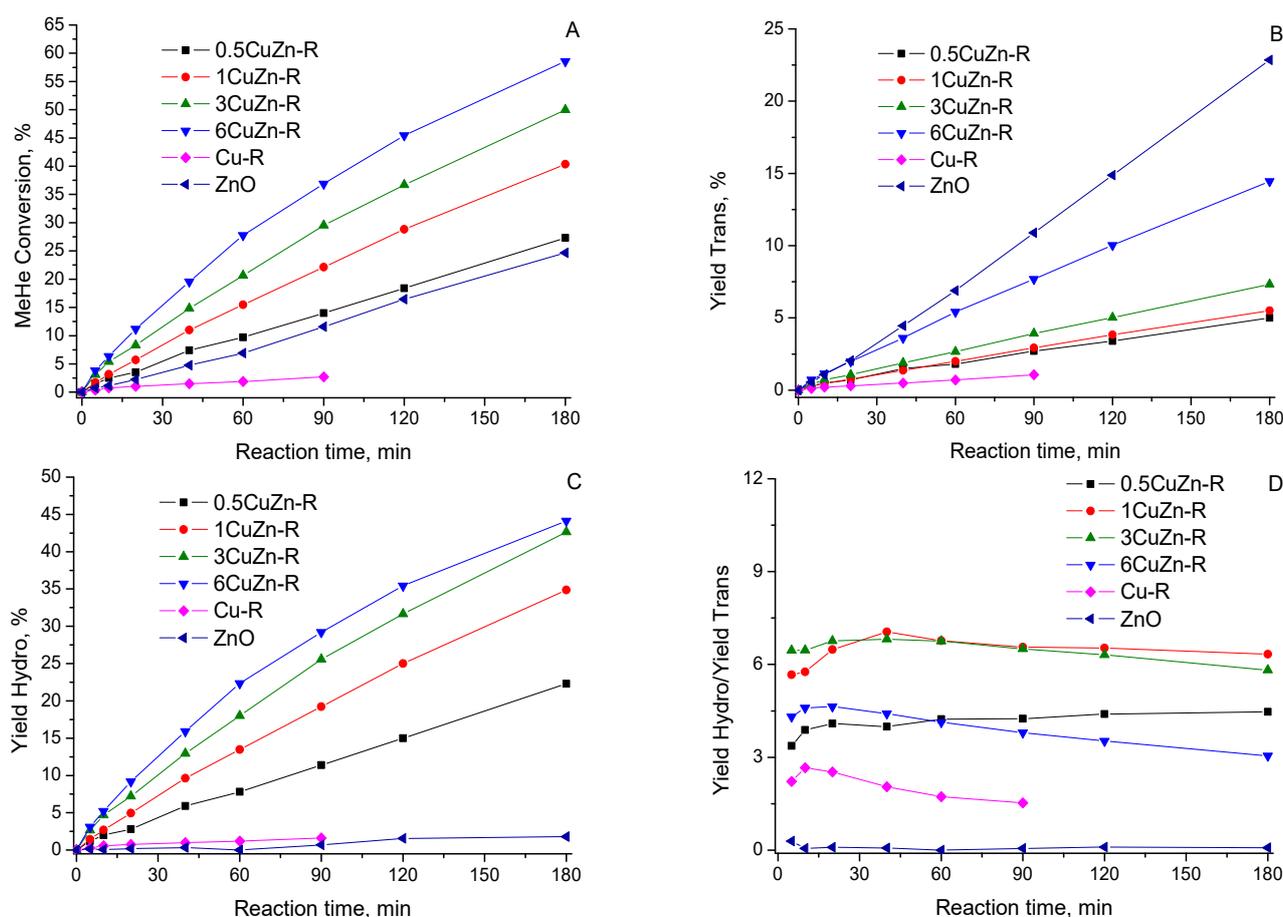


Figure S2. MeHe conversion observed during the conversion of MeHe+1-Heol mixture in presence of reduced CuZn catalysts with different Cu/Zn ratio as well as single phase ZnO and Cu catalysts. MeHe weight – 71.8 g, 1-Heol weight – 28.1 g (MeHe:1-Heol=2 mol:mol), $m_{cat}=1.5$ g, (in case of ZnO $m_{cat}=0.75$ g), $T=210$ °C, $p=100$ bar H_2 . (A); The yield of transesterification products. (B); The yield of hydrogenolysis products. (C); The ratio of (Yield Hydro/Yield Trans). (D)

Figure S2(A) shows that MeHe conversion increased with the growth of Cu/Zn ratio in the catalysts, and 6CuZn-R was the most active among the studied catalysts. Considering the performance of single-phase catalysts, MeHe conversion on ZnO was close to that observed on 0.5CuZn-R, i.e. CuZn catalyst with largest Zn content, while the performance of reduced Cu sample was the worst among all studied samples. The transformation of MeHe on a single-phase ZnO took place almost exclusively by transesterification reaction route (Figure S2(B)), while the contribution of hydrogenolysis step on this catalyst was only at the level of an experimental error (Figure S2(C)). On the other hand, the yield of both transesterification and hydrogenolysis products on Cu-R catalyst was very low. The results obtained for single-phase catalysts agrees well with our previous conclusions that transesterification between a methyl ether and a formed alcohol takes place with the participation of ZnO, while Cu catalyst has low activity in hydrogenolysis reaction in absence of the modifying and stabilizing role of ZnO.

In case of CuZn-R catalysts, a decrease in Cu/Zn ratio in the catalysts resulted in a decrease in both the yield of HeHe formed by transesterification route (Figure S2(B)) and the yield of 1-Heol which was additionally formed as a hydrogenolysis product (Figure S2(C)). A high “Yield Hydro” observed for 6CuZn-R could be explained by a high TOF_{MeHe} value calculated for this catalyst in MeHe conversion (Table 4 from the main text). Figure S2(C) also depicts that, in accordance with previous experiments on the conversion of both MeHe and HeHe (Figure 4(A) and Figure 6 from the main text), the high initial hydrogenolysis activity of 6CuZn-R gradually degraded with increasing reaction time. On the other hand, an increase in the “Yield Trans” with the growth of Cu/Zn ratio in the catalysts, i.e.

with a decrease in ZnO content, is surprising and hard to explain. The discrepancy between ZnO content in CuZn-R catalysts and their transesterification ability could be explained either by the different accessibility of ZnO particles for reactant molecules, or by the different specific transesterification activity of ZnO particles which could in turn be concerned with their size, surrounding, or the existence of a close contact between zinc and copper particles.

Figure S2(D) shows the relationship between the yields of products formed by hydrogenolysis and transesterification routes (Yield Hydro/Yield Trans) and the chemical composition of the catalysts. The Yield Hydro/Yield Trans ratio was close to zero for ZnO catalyst, which possessed negligible hydrogenolysis activity under the selected reaction conditions. On the other hand, 1CuZn-R and 3CuZn-R exhibited the largest hydrogenolysis activity. The initial good hydrogenolysis activity of 6CuZn-R degraded with increasing reaction time, resulting in a gradual decrease in the Yield Hydro/Yield Trans ratio. Finally, the single-phase Cu catalyst demonstrated a moderate Yield Hydro/Yield Trans ratio because of its low activity in both reaction routes.

3. The stability of Cu and ZnO species in CuZn catalysts in the repeated reaction cycles of MeHe hydrogenolysis.

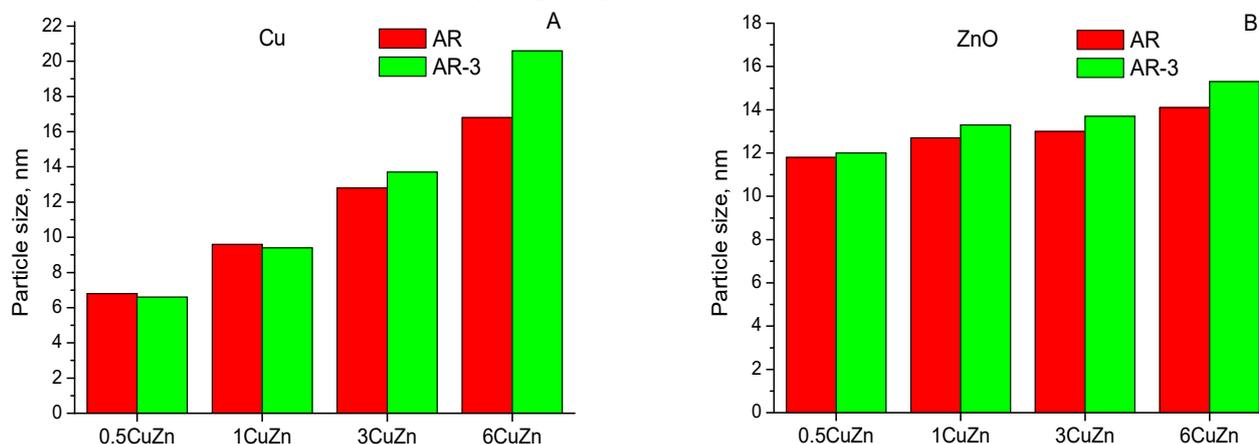


Figure S3. The comparison of Cu (A) and ZnO (B) particle size in spent catalysts after the first (AR) and the third (AR-3) catalytic runs.