

## Article

# Effect of Calcination Atmosphere and Temperature on the Hydrogenolysis Activity and Selectivity of Copper-Zinc Catalysts

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Received: 23 September 2018; Accepted: 7 October 2018; Published: 11 October 2018



Abstract: A series of CuZn catalysts with a Cu/Zn ratio of 1.6 was prepared by the calcination of a single precursor, CuZn-P consisting of an equimolar mixture of aurichalcite and zincian malachite, in three different calcination atmospheres (air, nitrogen, and hydrogen) at three temperatures (220, 350, and 500 °C). All catalysts were characterized by XRD and N<sub>2</sub>-physisorption to assess their phase composition, crystallite sizes and textural properties and tested in dimethyl adipate (DMA) hydrogenolysis in a batch reactor at 220 °C and 10 MPa H<sub>2</sub>. The XRD examination of these catalysts proved that both parameters, calcination temperature and atmosphere, affected the resulting phase composition of the catalysts as well as their crystallite sizes. In an oxidizing atmosphere, CuO and ZnO in intimate contact prevailed whereas in inert or reducing atmosphere both oxides were accompanied by Cu<sub>2</sub>O and Cu. The crystallite size of Cu<sub>2</sub>O and Cu was larger than the size of CuO and ZnO thus indicating a less intimate contact between the Cu-phases and ZnO in catalysts calcined in nitrogen and hydrogen. Catalysts prepared by calcination at 220 °C and CuZn catalyst calcined in the air at 350 °C significantly outperformed the other catalysts in DMA hydrogenolysis with a 59–78% conversion due to the small crystallite size and intimate contact between the CuO and ZnO phases prior to catalyst reduction. Despite the low DMA conversion (<30%), transesterification products were the main reaction products with overall selectivities of >80% over the catalysts calcined in nitrogen or hydrogen at least at 350 °C. The obvious change in the preferred reaction pathway because of the atmosphere calcination and temperature shows that there are different active sites responsible for hydrogenolysis and transesterification and that their relative distribution has changed.

**Keywords:** hydrogenolysis; transesterification; CuZn catalysts; calcination atmosphere; calcination temperature

## 1. Introduction

Over the past few decades, increasing attention has been paid to green chemistry principles to achieve a higher sustainability of chemical technologies. One of these principles is based on the application of highly efficient catalysts in industrial processes. However, their efficiency alone does not guarantee the overall technological sustainability as some catalyst productions use or produce harmful materials. This is the case of the traditional, highly efficient Adkins catalysts containing chromium that



have been used for the industrial hydrogenolysis of esters to alcohols since the 1950s [1–3]. Recently, copper-zinc catalysts have been shown to possess significant catalytic activity in the hydrogenolysis of biomass-derived esters [4–6] and could thus replace copper-chromium catalysts that do not meet the highest environmental standards.

Copper-zinc catalysts belong among widely studied catalysts due to a significant interest in the methanol synthesis from synthesis gas [7–9], as well as by the hydrogenation of carbon dioxide [10,11]. From a structural point of view, several studies have concluded that zinc oxide supports the adsorption of hydrogen on the copper surface and ensures the stabilization of the copper dispersion [7,12]. ZnO has also been suggested to act as a spacer between copper particles supporting high copper dispersion and thus maximizing the specific surface of copper [7,8,13]. This is of importance as Cu is the active component responsible for the hydrogenation and hydrogenolysis activity of catalysts. Nonetheless, the exact nature of the Cu active sites is still a matter of discussion even in the case of the most studied methanol synthesis [8] and it is not yet sufficiently described in hydrogenolysis catalysts. Recently, the formation of transesterification products during the hydrogenolysis of dimethyl adipate over a CuZnAl catalyst has been reported [6] and a reaction scheme has been proposed (Scheme 1). However, a clear understanding of the transesterification activity is still lacking. Moreover, due to the sensitivity of the copper-based catalysts to thermal treatment at elevated temperatures, the optimization and stabilization of the distribution of Cu active sites is challenging and studies dealing with the effect of calcination conditions are rather scarce [14].

Therefore, the present work is focused on a systematic study of the effect of three different calcination gas atmospheres, i.e., air, nitrogen, and hydrogen, on the structure and catalytic performance of catalysts obtained by the calcination of a precipitated CuZn catalyst precursor at three different temperatures (220, 350, and 500 °C) in these three calcination atmospheres. Particular attention is paid to the effect of the calcination on the relative activity of these CuZn catalysts in the hydrogenolysis and transesterification reactions in order to contribute to a better understanding of both catalytic functions.



**Scheme 1.** The proposed reaction network explaining the formation of the transesterification by-products during the hydrogenolysis of dimethyl adipate [6]. DMA is dimethyl adipate,  $1C_6$ MEol is methyl 6-hydroxyhexanoate, HDOL is hexane-1,6-diol,  $2C_6$ diME is 6-methoxy-6-oxohexyl methyl adipate,  $2C_6$ MEol is 6-hydroxyhexyl methyl adipate,  $2C_6$ diol is 6-hydroxyhexyl 6-hydroxyhexanoate,  $3C_6$ diME is bis(6-methoxy-6-oxohexyl) adipate,  $3C_6$ MEol is 6-hydroxyhexyl (6-methoxy-6-oxohexyl) adipate, and  $3C_6$ diol is bis(6-hydroxyhexyl) adipate.

## 2. Results and Discussion

#### 2.1. Catalyst Characterization

The Cu/Zn atomic ratio in the synthesized catalyst precursor determined by XRF was 1.6, i.e., very close to that expected from the chemical composition of the solution of copper and zinc nitrates used in the precipitation (1.5). Moreover, it was assumed that all catalyst samples prepared by different thermal treatments had the same chemical composition.

The phase composition of the catalyst precursor, as well as that of the final catalysts, was investigated by XRD. The XRD pattern of the as-prepared CuZn precursor (Figure 1) revealed that this sample was a mixture of two phases, zincian malachite ( $(Cu_{0.8} Zn_{0.2})_2(OH)_2CO_3$ ; Ref. Code No. 01-079-7851) and aurichalcite ( $Cu_2Zn_3(CO_3)_2(OH)_6$ ; Ref. Code No. 04-010-3227), found in almost equal amounts.

The XRD patterns of the catalysts prepared by calcination in static air at the three calcination temperatures (220, 350, and 500 °C) are compared with the XRD pattern of the catalyst precursor in Figure 1. When the catalyst precursor was treated at 220 °C, the phase composition did not change, although the intensity of the XRD reflexes decreased slightly. This can be attributed to the good thermal stability of zincian malachite and aurichalcite. It was reported that zincian malachite and aurichalcite are stable up to 270 °C and 360 °C, correspondingly [14,15]. When the calcination temperature was increased to 350 °C, the zincian malachite and aurichalcite crystalline domains present in the CuZn catalyst precursor decomposed completely and the CuO and ZnO crystalline particles were formed. A further increase in the calcination temperature to 500 °C did not change the phase composition of the catalyst anymore, i.e., the CuZn-500AS sample consisted exclusively of a mixture of CuO and ZnO. However, the intensity of the XRD reflexes notably increased, suggesting a growth of the crystallites size of both CuO and ZnO.



**Figure 1.** The XRD patterns of the catalysts prepared by the treatment of the CuZn precursor in static air at 220, 350, and 500  $^{\circ}$ C.

The XRD patterns of the catalysts prepared by calcination in nitrogen again at temperatures 220, 350, and 500 °C were compared with the XRD pattern of the catalyst precursor in Figure 2. Unlike in the case of treatment in static air at 220 °C, the thermal treatment of the CuZn-P in a nitrogen atmosphere at 220 °C (underflow conditions) resulted in a change in the phase composition of the prepared catalyst sample (CuZn-220N). Although the reflexes of zincian malachite and aurichalcite

are still present (Figure 2), they are accompanied by the reflexes of CuO and ZnO. This evidences that the thermal decomposition of the initial crystalline phases has started under these calcination conditions. This difference can be explained by the different experimental setups, in particular, by the flow conditions or the partial local overheating of the precursor sample inside the autoclave (the sample is in contact with the autoclave wall while the thermocouple measuring the temperature is not). An increase in the treatment temperature to  $350 \,^{\circ}$ C resulted in a total disappearance of the reflexes of zincian malachite and aurichalcite accompanied by an increase in the intensity of the reflexes of CuO and ZnO. Additionally, the reflexes belonging to Cu<sub>2</sub>O and Cu were identified in the XRD pattern of CuZn-350N as well (Figure 2). Because of the significant overlapping of the XRD reflexes of the different phases, only several characteristic reflexes are shown in Figure 2.

$$2Cu_2CO_3(OH)_2 \rightarrow 4CuO + 2CO_2 + 2H_2O \tag{1}$$

$$2CO_2 \rightarrow 2CO + O_2 \tag{2}$$

$$4CuO + 2CO \rightarrow 2Cu_2O + 2CO_2 \tag{3}$$



**Figure 2.** The XRD patterns of catalysts prepared by the treatment of the CuZn precursor in flowing nitrogen at 220, 350, and 500 °C.

The exclusive formation of CuO resulting from the calcination of malachite in air (Equation (1)) and the possible formation of Cu<sub>2</sub>O during the calcination of malachite in an inert atmosphere was reported previously [15]. It was explained by CO<sub>2</sub> decomposition to CO and subsequent reduction of CuO by CO (Equations (2) and (3)) [16]. The decomposition of both zincian malachite, and aurichalcite in nitrogen, by analogy with malachite, can be expected to yield Cu<sub>2</sub>O in addition to CuO. If CuO is reduced by CO originating from CO<sub>2</sub> to Cu<sub>2</sub>O, the consecutive reduction step, i.e., the reduction of Cu<sub>2</sub>O to Cu, is plausible as well. A further increase in the treatment temperature to 500 °C did not change the phase composition of the catalyst anymore, but the intensity of reflexes of all phases increased substantially due to the increased crystallite size of all phases. With a closer inspection of Figure 2, it can be established that the intensity of the reflexes corresponding to Cu<sub>2</sub>O and Cu increased more than those belonging to CuO and ZnO (Figure 2).

Finally, the catalyst precursor was also treated in flowing hydrogen at 220, 350, and 500 °C. The resulting XRD patterns are shown in Figure 3 together with the XRD pattern of the catalyst precursor. In contrast to the treatment in air and nitrogen at 220 °C, there are no reflexes of the initial hydroxycarbonate phases in the XRD pattern of the CuZn-220H, i.e., a catalyst obtained by treatment

in a hydrogen atmosphere at 220 °C. Instead, low-intensive reflexes of ZnO, CuO, Cu<sub>2</sub>O, and Cu appeared (Figure 3). As the treatment temperature increased from 220 °C to 500 °C, the intensity of the reflexes of the oxidic Cu phases declined while that of the metallic copper substantially increased (Figure 3). Simultaneously, the intensity of the reflexes of ZnO also increased. This can be attributed to the increase in the crystallite size of ZnO and Cu (discussed below) and to the gradual reduction of the oxidic Cu phases to metallic Cu.



**Figure 3.** The XRD patterns of catalysts prepared by the treatment of the CuZn precursor in flowing hydrogen at 220, 350, and 500 °C.

The XRD results demonstrate that 220 °C is a sufficient temperature to completely decompose hydroxycarbonates (zincian malachite and aurichalcite) in a hydrogen atmosphere, but not in air or nitrogen atmospheres. The lowered thermal stability of both hydroxycarbonate phases may be a consequence of a direct reduction of the hydroxycarbonate Cu species in zincian malachite and/or aurichalcite structures according to the proposed overall reaction (Equation (4)). This conclusion is further corroborated by the observed partial destruction of the hydroxycarbonate phase under nitrogen at 220 °C. The partial destruction is caused by the transformation of the inert atmosphere into a partially reducing atmosphere due to the formation of CO during the treatment.

$$2(Cu_{0.8}Zn_{0.2})_2CO_3(OH)_2 + 3.2 H_2 \rightarrow 3.2Cu + 0.8ZnO + CO_2 + 5.2H_2O$$
(4)

Nevertheless, Figure 3 also evidences that CuZn-220H still contained CuO in its composition after the calcination step (it can be considered as a reduction step at the same time), which is another distinctive feature of the experiment performed in hydrogen at 220 °C. This is rather unexpected since the reduction of CuO to metallic copper in CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> [17] or in CuO/ZnO [11] occurred at temperatures around 200 °C. On the other hand, the reduction of Cu<sup>2+</sup> in bulky CuO was reported to occur at 300 °C [11]. It was proposed that the low-temperature reduction of CuO to metallic Cu took place for highly dispersed copper oxide species while the bulky CuO was reduced at higher temperatures [15,17]. The presence of oxidic Cu species in CuZn-220H allows for the assumption that the treatment conditions considerably influenced the properties (oxidation state, dispersion, etc.) of the Cu atoms in the resulting catalyst sample. Indeed, dedicated experiments showed (Figure A1) that the treatment of the CuZn-350AS sample (which is a mixture of ZnO and CuO phases; see Figure 1) in a hydrogen atmosphere at 220 °C resulted in the total reduction of copper oxide to metallic copper. Moreover, the exclusive presence of the reflexes of metallic copper, i.e., without any oxidic phases

detected suggests that these metallic domains are not susceptible to an easy re-oxidation in the air. In contrast, the treatment of CuZn-P firstly in the air at 220 °C (yielding the CuZn-220AS sample) and then in hydrogen at the same temperature (Figure A1) resulted in the decomposition of zincian malachite and aurichalcite structures. The XRD pattern of CuZn-220AS-220H contained reflexes of CuO together with reflexes of metallic Cu at very low intensities. Thus, the existence of oxidic copper domains in the sample after a reductive treatment at 220 °C is undoubtedly a consequence of the sample preparation under specific conditions and their sequence.

The collected XRD patterns allowed for the calculation of the crystallite size of all phases detected in the catalysts using the Scherrer equation [18]. The sizes of the crystallites of zinc and copper compounds were calculated from the width of the corresponding diffraction lines that did not overlap with the lines belonging to other phases. As expected, the crystallite size depended on the pretreatment temperature and, more interestingly, on the calculation atmosphere (Table 1).

Sample	Particle Size, nm (2 Theta, Degrees)					
	ZnO (31.7)	CuO (38.7)	Cu <sub>2</sub> O (42.3)	Cu (43.3)		
220AS	ND <sup>1</sup>	ND	ND	ND		
220AS-220H <sup>2</sup>	7.3	7.3	8.7	10.2		
350AS	5.1	7.7	ND	ND		
350AS-220H <sup>2</sup>	12.5	ND	ND	18.1		
500AS	15.8	11.9	ND	ND		
220N	5.9	6.5	7.9	11.5		
350N	11	10.3	21	22.2		
500N	33.9	25.5	36	46.1		
220H	9.8	9.2	11.2	18.1		
350H	20	16.7	ND	23.4		
500H	34.7	ND	ND	33.2		

**Table 1.** The crystallite size of ZnO, CuO, Cu<sub>2</sub>O, and Cu present in the catalysts prepared by calcination in different atmospheres at different temperatures.

<sup>1</sup> ND stands for not detected; <sup>2</sup> After the reduction at 220 °C.

Due to the increasing pretreatment temperature in static air from 350 °C to 500 °C, the size of the ZnO and CuO crystallites increased from 5.1 nm and 7.7 nm to 15.8 and 11.9 nm, correspondingly. When the pretreatment was performed in a non-oxidizing atmosphere, either in nitrogen or in hydrogen, the size of the produced oxidic particles was larger compared to the corresponding experiments in static air (Table 1). Moreover, at a given temperature, the size of ZnO crystallites was larger in the catalysts prepared by calcination in nitrogen or hydrogen in comparison with those prepared in air (Table 1). This allows for the suggestion of a mutual stabilization of the CuO and ZnO domains if these are in intimate contact with each other. This conclusion is further supported by the larger size of the Cu crystallites obtained by direct reduction (calcination in hydrogen) than those obtained by calcination in air followed by reduction at 220  $^{\circ}$ C (Table 1). In addition, the size of metallic copper increased in comparison with the size of its oxidic precursors which indicates copper sintering during the reduction step. It is interesting to note that (i) the catalysts reduced after previous calcination in air, (ii) catalysts obtained by calcination in nitrogen (copper formed due to reduction by in-situ formed CO) and (iii) catalysts prepared by calcination in hydrogen (i.e., by direct reduction) exhibit a common linear dependency between the CuO crystallite size and the resulting Cu crystallite size (Figure 4). This might indicate that Cu is formed during the calcination of the hydroxycarbonate precursors either via CuO or that the formation of both crystallites is related in another way.



**Figure 4.** A relationship between the CuO and Cu crystallites size in catalyst samples prepared by calcination in air ( $\Box$ ), nitrogen ( $\Delta$ ) and hydrogen ( $\bigcirc$ ) at different temperatures.

The calcination atmosphere and temperature significantly affected the textural properties of the final catalysts. The results are summarized in Table 2. Among the samples calcined in air, CuZn-350AS possessed the best textural properties with respect to the BET surface, the external surface, pore volume, and average nanoparticle size. The CuZn-220AS had only slightly worse parameters compared to CuZn-350AS despite their substantially different phase composition. This could be attributed to the fact that CuZn-220AS was a mixture of hydroxycarbonates rather than of oxides. The increase in the calcination temperature to 500 °C resulted in a dramatic decrease in the textural properties of CuZn-500AS. On the other hand, the trend in the change in all characteristics observed for the samples prepared in nitrogen and hydrogen is more unambiguous. The BET surface, the external surface, and the pore volume substantially decreased while the average nanoparticle size, accordingly, increased with the increasing calcination temperature. It should also be noted that the samples prepared in hydrogen had worse adsorption characteristics, except for the micropore surface, compared with the similar samples prepared in nitrogen. Besides, Table 2 evidences that the pore diameter of differently prepared catalysts was approximately the same in the range of 13–39 nm and showed no dependence on either the atmosphere or calcination temperature.

Sample	BET Surface,	t-Plot Surface, $m^2 \cdot g^{-1}$		BJH Pore	BIH Pore	Average
	$m^2 \cdot g^{-1}$	Micropore	External	Volume, cm <sup>3</sup> ·g <sup>−1</sup>	Diameter, nm	Nanoparticle Size, nm
CuZn-220AS	49	5.1	43.9	0.342	27	122
CuZn-350AS	62	1.3	61.1	0.463	25	96
CuZn-500AS	17	0.1	16.5	0.084	23	364
CuZn-220N	65	0	78.3	0.4	21	89
CuZn-350N	32	4.7	27.6	0.274	39	186
CuZn-500N	8	0.8	7.5	0.021	13	722
CuZn-220H	26	3.1	22.7	0.194	31	233
CuZn-350H	14	0.6	13.5	0.089	27	423
CuZn-500H	NM <sup>1</sup>					

**Table 2.** The textural properties of the CuZn catalysts prepared by the calcination of the CuZn precursor in air, nitrogen, and hydrogen at 220, 350, and 500 °C.

<sup>1</sup> NM stands for not measured.

#### 2.2. Activity and Selectivity of the Catalysts

Figure 5 depicts the dependency of the DMA conversion on the pretreatment conditions (i.e., different calcination atmosphere and temperature) applied to the synthesized CuZn-P precursor. CuZn-220AS prepared by a mild heating in static air possessed a reasonable activity in the reaction with DMA; the DMA conversion reached 64% after 2 h. When the calcination temperature was increased to 350 °C, the catalytic performance of the catalyst further improved; the DMA conversion amounted to 78% after 2 h (Figure 5). The observed increase is in agreement with the improvement in the textural properties of CuZn-220AS and CuZn-350 AS (Table 2). Additionally, the phase composition of the calcined catalysts after reduction has to be considered as well. The catalyst CuZn-220AS, if exposed to hydrogen at 220 °C for 2 h, still contained Cu in the oxidic state (Figure 4, sample CuZn-220AS-220H). On the other hand, the XRD pattern of this catalyst after the reaction (will be discussed further) revealed the presence of only metallic Cu clusters. This suggests the occurrence of a subsequent reduction of the oxidic Cu species during the reaction. In contrast, the catalyst CuZn-350AS exclusively contained metallic Cu clusters after the reduction step, so no additional activation during the reaction was necessary. This difference in the state of Cu in the catalysts, although inexplicable at the moment, could explain the difference in the catalytic performance of CuZn-220AS and CuZn-350AS together with their different textural properties. A further increase in the calcination temperature in air to 500 °C resulted in a decrease in the activity of the catalyst CuZn-500AS with the DMA conversion of 43% after 2 h (Figure 5).



**Figure 5.** The DMA conversion observed on the CuZn catalysts in dependence on the temperature of their treatment in air (black line), N<sub>2</sub> (red line), and H<sub>2</sub> (blue line). Samples calcined at T = 220 °C ( $\bigcirc$ ), 350 °C ( $\square$ ), 500 °C ( $\Delta$ ).

The observed decrease in conversion can be attributed to the increase in the size of the copper crystallites determined from the XRD patterns (Table 1). The increase in the calcination temperature caused an increase in the size of copper crystallites leading to a decrease in the number of available catalytically active centers. A similar dependence of the catalytic performance of Cu-containing catalysts on the particle size of copper being influenced by the calcination temperature was also reported for the hydrogenolysis of ethyl acetate to ethanol [4]. In contrast, Peng Yuan et al. [5] observed an increase in the DMA conversion over a Cu–Zn–Al catalyst as the calcination temperature was increased from 400  $^{\circ}$ C to 500  $^{\circ}$ C.

The catalysts prepared by calcination in nitrogen and hydrogen also showed a trend of decreasing the DMA conversion with the increasing calcination temperature. For CuZn catalysts prepared by calcination in nitrogen, the DMA dropped significantly (from 59 to 3%) when the calcination

temperature was increased from 220 °C to 500 °C (Figure 5). The effect of the hydrogen calcination atmosphere was even more pronounced. The DMA conversion decreased from 63% to a negligible 1% when the calcination temperature was increased from 220 °C to 500 °C. The physicochemical characterization of the catalysts allows the attributing of this behavior to the increase in the Cu crystallite size with increasing calcination temperature and to the worse textural properties of catalysts prepared by calcination at high temperatures. The dependence of the conversion on crystallite size is obvious when the DMA conversion is plotted as a function of CuO or Cu crystallites (Figures 6 and A2).



**Figure 6.** A correlation between the DMA conversion (after 120 min. of the reaction) and the size of CuO crystallites in the prepared CuZn catalysts.  $\Box$ : calcined in air,  $\Delta$ : calcined in nitrogen,  $\bigcirc$ : calcined in hydrogen.

The observed correlation between the catalytic performance of CuZn catalysts prepared in the present study and the size of the Cu domains can be expected since the performance of the Cu-containing catalysts in different reactions has been repeatedly shown to depend on copper particle size [5,11,17]. Nevertheless, the treatment of the starting precursor in air, on the one hand, and in nitrogen or hydrogen, on the other hand, introduces some unique (previously not described) features to the performance of the CuZn hydrogenolysis catalyst. Regardless of the atmosphere used, all catalysts which were thermally treated at 220 °C exhibited approximately the same catalytic activity. The DMA conversion was in the range 59–64% (Figure 5) despite their phase composition after calcination differing significantly (Table 1). Moreover, the comparison of catalytic results with the physicochemical properties of the prepared catalysts exhibits no clear correlation between the catalytic performance of the catalysts and their textural properties.

On the other hand, catalytic results suggest that the high DMA conversion over catalysts prepared at 220 °C is observed provided that the samples possess small-size copper crystallites (Table 1). An increase in the calcination temperature to 350 °C resulted in an increase in the DMA conversion to 78% for CuZn-350AS while the activity of CuZn-350N and CuZn350H markedly decreased. According to XRD, CuZn-350AS represents a mixture of ZnO and CuO whereas the other samples contain notable amounts of Cu<sub>2</sub>O and Cu besides CuO and ZnO. The crystallite size of Cu<sub>2</sub>O and Cu is significantly larger than that of CuO and ZnO and they are plausibly present as separate phases that are not in intimate contact with the ZnO phase. This difference in the phase composition of the samples allows for the suggestion that an intimate contact between the CuO and ZnO crystallites because of the thermal treatment could be an important factor that stabilizes the small size of the Cu domains. Consequently, a high activity of CuZn catalysts is achieved. When calcining in air, the increase in the calcination temperature from 220 °C to 350 °C resulted in a complete destruction of the zincian malachite and aurichalcite structures. This led to an increased number of CuO and ZnO crystallites, thus, promoting the probability of close contact between the two phases. Additionally, the very small

size of ZnO crystallites (Table 1) could also contribute to the high dispersion of the CuO domains. In contrast, the presence of the Cu<sub>2</sub>O and Cu crystallites in samples prepared in N<sub>2</sub> and H<sub>2</sub> reduced the probability of the necessary interaction between CuO and ZnO. As a result, the number of potentially active sites formed on the interface between the CuO and ZnO domains after the reduction differs for catalysts prepared by the calcination in different atmospheres. Additionally, the existence of the said interfaces contributes to the stabilization of the Cu crystallites in ZnO surroundings. As a result, CuZn-350AS has a higher BET surface area, external surface, and pore volume with lower crystallites size values than CuZn-350N and CuZn-350H. As can be deduced from Table 1, the absence of intimate CuO-ZnO contact resulted in a more facile sintering of both the Cu and Zn domains at elevated temperatures. Consequently, the DMA conversion over CuZn-350AS was the highest among all catalysts (78%), while the DMA conversion observed over CuZn-350N and CuZn-350H was much lower, i.e., 32% and 17%, respectively. The significantly lower conversion over CuZn-350H in comparison with CuZn-350N is the consequence of a more extensive reduction of CuZn-350H during calcination and, hence, the lower probability to stabilize the CuO domains by intimate contact with ZnO. Consequently, the CuO and ZnO crystallites are approximately 17-20 nm large in CuZn-350H whereas only 10–11 nm in CuZn-350N (Table 1).

As reported previously [6], CuZn catalysts catalyze not only hydrogenolysis, but highermolecular-weight products originating from transesterification reactions between DMA, 1,6-hexanediol (1,6-HDO), and partially hydrogenolyzed DMA (1HMEol) are also formed. These transesterification products consist of products with two C<sub>6</sub> backbones in their molecules (denoted H2) or with three C<sub>6</sub> backbones in their molecules (denoted H3). Thus, the selectivity to and yields of different products allow for obtaining additional important information on the performance of catalysts particularly with respect to the origins of the transesterification activity of the CuZn catalysts. Figure 7 depicts the selectivity towards reaction products formed by DMA hydrogenolysis over catalysts prepared by the thermal activation of CuZn-P in air. Regardless, the calcination temperature selectivity to the reaction products observed over the three CuZn-TAS catalysts followed the same trend as a function of DMA conversion. To maintain readability of the graph, the selectivities over all CuZn-TAS catalysts were not distinguished according to the calcination temperature (Figure 7).



**Figure 7.** The change of selectivity to the reaction products in dependence on the DMA conversion observed over the catalysts prepared by the calcination of the precursor, CuZn-P, in the air at 220, 350, and 500 °C. 1HMEol is methyl 6-hydroxyhexanoate; 1,6-HDO is hexane-1,6-diol; H2 is the sum of 6-methoxy-6-oxohexyl methyl adipate, 6-hydroxyhexyl methyl adipate, and 6-hydroxyhexyl 6-hydroxyhexanoate; and H3 is the sum of bis(6-methoxy-6-oxohexyl) adipate, 6-hydroxyhexyl (6-methoxy-6-oxohexyl) adipate, and bis(6-hydroxyhexyl) adipate.

The composition of the main reaction products and their tendency to change with the increasing DMA conversion is consistent with the results from our previous work [6]. 1HMEol is evidently a primary product formed by the hydrogenolysis of only one ester group of the two present in the DMA. Its selectivity approached 100% at DMA conversion close to zero. Subsequently, 1HMEol can be transformed either by the hydrogenolysis of the second ester group yielding 1,6-HDO or by participating in transesterification reactions yielding bulky H2 and H3 molecules (for structures and chemical names, see Scheme 1). The hydrogenolysis of the second ester group in the DMA, i.e., the ester group in 1HMEol, also proceeded very fast on the catalysts prepared by calcination in air. Consequently, the selectivity to 1,6-HDO reached 20% at a DMA conversion as low as 12%. However, once 1HMEol and 1,6-HDO were formed, the transesterification reactions involving DMA, 1HMEol, and/or 1,6-HDO became possible and resulted in a formation of bulky compounds with either two or three "hexane backbones" in their molecule, denoted as H2 and H3 (for structures, see Scheme 1). During the reaction, the formation of the heavy H2 and H3 compounds became prevalent. Therefore, at DMA conversion of about 80%, the selectivity to H2 and H3 attained 44% and 21%, respectively. In addition, other reaction products, including cyclic ones (due to intramolecular transesterification), have also been identified among the reaction products. Their amount was small and they were excluded from further consideration. It can be inferred that the transesterification reactions are preferred to the second ester group hydrogenolysis under the studied reaction conditions as the selectivity to 1,6-HDO increased at a much more moderate rate with the increasing DMA conversion than the selectivity to the H2 and H3 products.

It has been reported that the hydrogenolysis of both ester functions in the DMA molecule does not occur at the same rate [5,19]. Hence, a ratio between the selectivities to HDO and the sum of the H2 and H3 products can help in evaluating the contribution of different reaction routes to the total composition of the reaction products. The ratio  $S_{HDO}/S_{H2+H3}$  observed for CuZn catalysts calcined in air varied only slightly for the three calcination temperatures; it was in the range of 0.61–0.94 at a DMA conversion  $\approx$ 10%. This shows that the ratio between the active sites responsible for hydrogenolysis and transesterification, respectively, is approximately the same in these catalysts and does not change significantly due to different calcination temperature in air.

In the case of catalysts prepared by calcination in nitrogen and hydrogen at 220 °C (CuZn-220N and CuZn-220H, respectively), the maximum yield of 1HMEol reached ca. 10–12% at a DMA conversion of ca. 40%. The same maximum yield of 1HMEol was also obtained for all three catalysts prepared by calcination in air (Figure 8(1A,2A,3A)), suggesting that all catalysts prepared by calcination at 220 °C have a similar distribution of the Cu active sites regardless of the calcination atmosphere. Consequently, the  $S_{HDO}/S_{H2+H3}$  calculated for CuZn-220N and CuZn-220H at DMA conversion  $\approx$ 10% was 0.77 and 0.7, correspondingly, which is within the range of values observed for the catalysts prepared by the calcination in air. Similar to the air-calcined CuZn catalysts, the selectivity to H2 and H3 increased markedly with the increase in the DMA conversion for CuZn-220N and CuZn-220H catalysts, implying the secondary nature of H2 and H3 formation.

A different selectivity character was observed in the case of samples prepared by the calcination of the CuZn-P precursor at 350 and 500 °C in nitrogen or hydrogen. The yields of the 1HMEol were minor—the maximum yield of 1HMEol was achieved over CuZn-350N and amounted to 2% at a DMA conversion of 30%. This is significantly less than the samples calcined at 220 °C in nitrogen, hydrogen, or in air (ca. 10–12% yield at a 30% DMA conversion). The 1,6-HDO yields were virtually 0%, which is again dramatically lower than the other catalysts that yielded 4–6% HDO at comparable conversions (Figure 8(1B,2B,3B)). Surprisingly, the esters (H2 and H3 products) requiring 1HMEol and/or HDO in addition to DMA were the prevailing reaction products. At a given conversion, their yield significantly exceeded the yield of esters formed over the CuZn catalysts calcined at 220 °C (in all atmospheres) and all catalysts calcined in air (i.e., calcined at 220, 350, or 500 °C); see Figure 8(1C,2C,3C,1D,2D,3D). It can be inferred that the calcination temperature in a non-oxidizing atmosphere had a severe impact on the hydrogenolysis activity of the CuZn catalysts, as the S<sub>HDO</sub>/S<sub>H2+H3</sub> dropped to values as low as 0.002 for catalysts calcined at 350 °C in N<sub>2</sub> or H<sub>2</sub>. The results, thus, provide strong evidence that the hydrogenolysis of the methyl ester function and the transesterification reaction leading to the formation of bulky molecules, H2 and H3, occur on different active sites. Obviously, both the calcination atmosphere and temperature strongly affect the performance of the CuZn catalysts. The identification (and possibly also quantification) of the active sites, however, remains a task for forthcoming studies.



**Figure 8.** The change of the yield of reaction products (**A**: 1HMEol, **B**: HDO, **C**: H2, **D**: H3) with a dependence on the DMA conversion observed over the samples prepared by the thermal treatment of CuZn-P in air (1), nitrogen (2) and hydrogen (3).

## 3. Materials and Methods

A CuZn precursor with the copper/zinc molar ratio of 1.6 was prepared by a co-precipitation method based on the neutralization of a starting acidic solution with a basic precipitating agent. For the synthesis of the precursor, a glass beaker was filled with 200 mL of distilled water and heated to T = 60 °C under stirring at 600 RPM. An aqueous solution (0.5 M) containing Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (99.0%, Penta, s.r.o., Prague, Czech Republic), Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (99.6%, Lach:Ner, s.r.o., Neratovice,

Czech Republic), and an aqueous solution (0.5 M) of Na<sub>2</sub>CO<sub>3</sub> (99.4%, Lach:Ner, s.r.o., Neratovice, Czech Republic) used as the precipitant were dosed simultaneously dropwise to keep the pH value in the beaker in the range of  $7 \pm 0.1$ . The temperature and stirring rate were kept constant at 60 °C and 600 RPM, correspondingly, during the precipitation. The resulting suspension was aged under stirring for 90 min which caused an increase in the pH value to 7.6–7.7. The prepared precipitate was then filtered using a vacuum pump, washed with plenty of distilled water, and finally dried at 70 °C overnight.

To prepare a series of catalysts for the investigations, the starting CuZn precursor denoted as CuZn-P (fine powder, 1 g used for each experiment) was thermally treated either in an oven in static open air or in a Parr autoclave in a flow of either nitrogen (99.99% SIAD Czech, s.r.o., Prague, Czech Republic) or hydrogen (99.9% SIAD Czech, s.r.o, Prague, Czech Republic). The thermal activation of the precursor in each of the gas atmospheres was performed at 220, 350, and 500 °C for 2 h. The prepared samples were denoted as CuZn-TAS, CuZn-TN, and CuZn-TH, where *T* stands for the temperature of the heat treatment (calcination) while AS, N, and H stand for static air, flowing nitrogen and hydrogen used as a gas atmosphere, respectively. For example, CuZn-350AS denotes a catalyst prepared by the calcination of the precursor, CuZn-P, at 350 °C in an air atmosphere.

The copper and zinc content in the as-prepared CuZn-P sample were determined by XRF using a spectrometer ARL 9400 XP equipped with a rhodium lamp (Thermo ARL, Ecublens, Switzerland). The phase composition of the CuZn catalysts and the size of the crystallites of the relevant phases present in the catalysts were determined by X-Ray diffraction using a diffractometer PANanalytical X'Pert3 Powder and Cu K $\alpha$  radiation (PANanalytical, Eindhoven, The Netherlands). The XRD patterns were recorded in a range of  $2\theta = 5-90^{\circ}$ . The particle sizes were calculated using Scherrer's equation. Reflections at  $2\theta = 31.8^{\circ}$ ,  $36.2^{\circ}$ , and  $38.6^{\circ}$  were used for the particle size calculations of the ZnO, Cu, and CuO crystallites, respectively. Equilibrium adsorption isotherms of nitrogen were measured at 77 K using a static volumetric adsorption system (TriFlex analyzer, Micromeritics, Norcross, GA, USA). The samples were degassed at 473 K (12 h) prior to an N<sub>2</sub> adsorption analysis, in order to obtain a clean surface. The adsorption isotherms were fitted using the Brunauer-Emmett-Teller (BET) method for the specific surface area, the t-plot method for the external specific surface area, and the BJH method for the distribution of mesopores.

The hydrogenolysis of dimethyl adipate (>99%, Sigma-Aldrich, s.r.o., Prague, Czech Republic) was carried out in a Parr SS autoclave with a reactor volume of 300 mL using the prepared CuZn catalysts. Prior to the catalytic tests, all catalysts (1 g) were reduced in situ in the autoclave at 220 °C using flowing hydrogen (H<sub>2</sub> 99.9%, SIAD Czech, s.r.o., Prague, Czech Republic) at atmospheric pressure for 1 h. After the catalyst reduction, the temperature in the autoclave was decreased to below 100 °C and the reactor was loaded with 50 mL of dimethyl adipate (DMA) by a peristaltic pump (i.e., the autoclave with the reduced catalyst was not opened to avoid reoxidation of the catalyst). After that, the temperature in the autoclave was gradually increased to  $T = 210 \,^{\circ}$ C. Then, the hydrogen pressure was increased to 10 MPa and the catalytic experiment was initiated by starting the stirring of the reaction mixture (DMA with a catalyst) at 600 RPM. Liquid reaction products were periodically withdrawn from the autoclave, centrifuged, and analyzed by a GC (Agilent 6890N, HPST, s.r.o., Prague, Czech Republic) equipped with a FID and non-polar column (ULTRA 1, 0.32 mm internal diameter, 20 m length). The DMA conversion was calculated according to Equation (5). Due to the absence of cracking reactions, the C6 backbone present in the DMA molecule, as well as in the reaction products, was used to calculate the product selectivity (Equation (6)). Methanol (also a reaction product) was excluded from these calculations.

$$conversion_{DMA} = \frac{n_{DMA,i} - n_{DMA,t}}{n_{DMA,i}}$$
(5)

where  $n_{DMA}$  is the number of DMA moles in the reaction mixture, where *i* stands for the initial number of DMA moles and *t* stands for the number of DMA moles at the sampling time.

$$S_{x,t} = \frac{n_{x,t} - n_{x,i}}{\sum n_{products \ 1C6 \ backbone} + 2 \ \sum n_{products \ 2C6 \ backbones} + 3 \ \sum n_{products \ 3C6 \ backbones}} \tag{6}$$

where  $S_{x,t}$  is the selectivity to product x at time t of the experiment,  $n_x$  is the number of moles of product x in the starting/initial mixture (index i) or at the time of sampling (index t),  $n_{products yC6 backbone}$  refers to the number of product moles having one (y = 1), two (y = 2) or three (y = 3) C<sub>6</sub> backbones in their molecules.

## 4. Conclusions

The results from the present study show that starting from the same CuZn hydroxycarbonate precursor, it is possible to prepare samples greatly varying in physicochemical properties and catalytic performance. This can be achieved by the thermal treatment of the precursor using different atmospheres (air, nitrogen, and hydrogen) and calcination temperatures (220, 350, and 500 °C). Both calcination parameters affected the resulting phase composition of the catalysts as well as their crystallite size. In an oxidizing atmosphere, a mixture of CuO and ZnO was produced with increasing crystallite size as the calcination temperature grew. In contrast, in inert or reducing atmospheres, both oxides were accompanied by Cu<sub>2</sub>O and Cu. The crystallite sizes of Cu<sub>2</sub>O and Cu were larger than the sizes of CuO and ZnO, thus indicating a less intimate contact between the Cu-phases and ZnO in catalysts calcined in nitrogen and hydrogen. All three catalysts calcined in different atmospheres at T = 220 °C demonstrated good activity, resulting in a DMA conversion of 59–63%. The increase in the calcination temperature to 350 °C resulted in a growth of the DMA conversion to 78%, observed for the sample prepared in the oxidizing atmosphere. This is explained by the small crystallite size and intimate contact between the CuO and ZnO phases prior to the catalyst reduction. In contrast, the DMA conversion notably decreased over the samples prepared by the calcination in nitrogen or hydrogen at higher temperatures. This is explained by the decreased number of potentially active sites formed on the interfaces between the CuO and ZnO domains after the reduction and the lower stabilization of Cu crystallites in the ZnO surrounding. As a result, the DMA conversion decreased to a negligible 1% observed for samples calcined in N<sub>2</sub> and H<sub>2</sub> at 500 °C.

Calcination parameters used for the catalyst preparation greatly influenced not only DMA conversion but also product selectivity. The reaction over the air-calcined samples yielded 1,6-hexanediol with selectivity exceeding 20% at DMA conversion >10% independent of the calcination temperature. In contrast, the catalysts calcined in nitrogen or hydrogen at 350 and 500 °C exhibited selectivity to 1,6-hexanediol below 2% at DMA conversion ranging from 1% to 30%. Transesterification products (demoted H2 and H3) were the main reaction products with overall selectivities of >80% in these cases. The observed change in the catalytic performance of samples prepared by calcination in N<sub>2</sub> and H<sub>2</sub> allowed for suggesting that different active sites are responsible for the hydrogenolysis and transesterification reaction procedure applied to the starting CuZn precursor.

Author Contributions: Conceptualization, Methodology and Writing—original draft preparation, O.K. and D.K.; Investigation—experiments and analyses, O.K, J.A., V.P. and M.L.; Writing—review and editing, J.A., V.P. and D.K.

Funding: This research was funded by the Czech Science Foundation (project No. GA17-05704S).

Acknowledgments: This work was realized within the Operational Programme Prague—Competitiveness (CZ.2.16/3.1.00/24501) and "National Program of Sustainability" (NPU I LO1613) MSMT-43760/2015.

Conflicts of Interest: The authors declare no conflict of interest.

## Appendix A



**Figure A1.** The XRD patterns of catalyst samples prepared by the treatment of the CuZn precursor in static air at 220 and 350 °C followed by the treatment in a hydrogen at T = 220 °C.



**Figure A2.** A correlation between the DMA conversion and the size of the Cu crystallites in the prepared CuZn catalysts.  $\Box$ : calcined in air,  $\Delta$ : calcined in nitrogen,  $\bigcirc$ : calcined in hydrogen.

## References

- 1. Adkins, H.; Folkers, K. The catalytic hydrogenation of esters to alcohols. *J. Am. Chem. Soc.* **1931**, *53*, 1095–1097. [CrossRef]
- 2. Turek, T.; Trimm, D.L. The catalytic hydrogenolysis of esters to alcohols. *Catal. Rev.-Sci. Eng.* **1994**, *36*, 645–683. [CrossRef]
- 3. Adkins, H. Catalytic hydrogenation of esters to alcohols. Org. React. 1954, 8, 1–27.
- 4. Zhu, Y.-M.; Shi, L. Zn promoted Cu–Al catalyst for hydrogenation of ethyl acetate to alcohol. *J. Ind. Eng. Chem.* **2014**, *20*, 2341–2347. [CrossRef]

- Yuan, P.; Liu, Z.; Hu, T.; Sun, H.; Liu, S. Highly efficient Cu–Zn–Al catalyst for the hydrogenation of dimethyl adipate to 1,6-hexanediol: Influence of calcination temperature. *React. Kinet. Mech. Catal.* 2010, 100, 427–439. [CrossRef]
- Kubička, D.; Aubrecht, J.; Pospelova, V.; Tomášek, J.; Šimáček, P.; Kikhtyanin, O. On the importance of transesterification by-products during hydrogenolysis of dimethyl adipate to hexanediol. *Catal. Commun.* 2018, *111*, 16–20. [CrossRef]
- Zander, S.; Kunkes, E.L.; Schuster, M.E.; Schumann, J.; Weinberg, G.; Teschner, D.; Jacobsen, N.; Schloegl, R.; Behrens, M. The Role of the Oxide Component in the Development of Copper Composite Catalysts for Methanol Synthesis. *Angew. Chem. Int. Ed.* 2013, *52*, 6536–6540. [CrossRef] [PubMed]
- Behrens, M.; Studt, F.; Kasatkin, I.; Kuehl, S.; Haevecker, M.; Abild-Pedersen, F.; Zander, S.; Girgsdies, F.; Kurr, P.; Kniep, B.-L.; et al. The Active Site of Methanol Synthesis over Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> Industrial Catalysts. *Science* 2012, 336, 893–897. [CrossRef] [PubMed]
- 9. Behrens, M.; Kissner, S.; Girsgdies, F.; Kasatkin, I.; Hermerschmidt, F.; Mette, K.; Ruland, H.; Muhler, M.; Schloegl, R. Knowledge-based development of a nitrate-free synthesis route for Cu/ZnO methanol synthesis catalysts via formate precursors. *Chem. Commun.* **2011**, *47*, 1701–1703. [CrossRef] [PubMed]
- Fujita, S.-I.; Moribe, S.; Kanamori, Y.; Kakudate, M.; Takezawa, N. Preparation of a coprecipitated Cu/ZnO catalyst for the methanol synthesis from CO<sub>2</sub>—Effects of the calcination and reduction conditions on the catalytic performance. *Appl. Catal. A* 2001, 207, 121–128. [CrossRef]
- 11. Natesakhawat, S.; Lekse, J.W.; Baltrus, J.P.; Ohodnicki, P.R.; Howard, B.H.; Deng, X.; Matranga, C. Active Sites and Structure-activity Relationships of Copper based Catalysts for Carbon Dioxide Hydrogenation to Methanol. *ACS Catal.* **2012**, *2*, 1667–1676. [CrossRef]
- Wang, S.; Liu, H. Selective hydrogenolysis of glycerol to propylene glycol on Cu–ZnO catalysts. *Catal. Lett.* 2007, 117, 62–67. [CrossRef]
- 13. Hu, Q.; Fan, G.; Yang, L.; Li, F. Aluminum-doped zirconia-supported copper nanocatalysts: Surface synergistic catalytic effects in the gas-phase hydrogenation of esters. *Chemcatchem* **2014**, *6*, 3501–3510. [CrossRef]
- 14. Schumann, J.; Tarasov, A.; Thomas, N.; Schlögl, R.; Behrens, M. Cu, Zn-based catalysts for methanol synthesis: On the effect of calcination conditions and the part of residual carbonates. *Appl. Catal. A* **2016**, *516*, 117–126. [CrossRef]
- 15. Millar, G.J.; Holm, I.H.; Uwins, P.J.R.; Drennan, J. Characterization of precursors to methanol synthesis catalysts Cu/ZnO system. *J. Chem. Soc. Faraday Trans.* **1998**, *94*, 593–600. [CrossRef]
- 16. Seciuin, M.K. Thermogravimetric and differential thermal analysis of malachite and azurite in inert atmospheres and in air. *Can. Mineral.* **1975**, *13*, 127–132.
- 17. Qi, G.-X.; Zheng, X.-M.; Fei, J.-H.; Hou, Z.-Y. A novel catalyst for DME synthesis from CO hydrogenation 1. Activity, structure and surface properties. *J. Mol. Catal. A Chem.* **2001**, *176*, 195–203. [CrossRef]
- 18. King, H.P.; Alexander, L.E. X-ray Diffraction Procedures, 2nd ed.; Wiley: New York, NY, USA, 1973.
- 19. Santos, S.M.; Silva, A.M.; Jordão, E.; Fraga, M.A. Hydrogenation of dimethyl adipate over bimetallic catalysts. *Catal. Commun.* **2004**, *5*, 377–381. [CrossRef]



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