Unravelling the Structural Modification (Meso-Nano-) of Cu/ZnO-Al₂O₃ Catalysts for Methanol Synthesis by the Residual NaNO₃ in Hydroxycarbonate Precursors

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Abstract: The effects of residual NaNO₃ on the modification of Cu/ZnO-Al₂O₃ catalysts have been extensively documented, but the modification mechanism is so far unclear. This work studies in detail the influence of the residual sodium nitrate present in the hydroxycarbonate precursors on their decomposition during calcination and how it affects to the formation and configuration of the final active sites of the Cu/ZnO-Al₂O₃ catalysts. Different samples with varying sodium content after washing (from 0.01 to 7.3 wt%) were prepared and studied in detail after calcination and reduction steps. The results of this work demonstrated that NaNO₃ affects the decomposition mechanism of the hydroxycarbonate precursors during calcination and produces its decarbonation at low temperature. The enhancement of the decarbonation by NaNO₃ leads to segregation and crystallization of CuO and ZnO with loss of mesostructure and surface area in the calcined catalysts. The loss of mesostructure in calcined catalysts affects the subsequent reduction step, decreasing the reducibility and damaging the nanostructure of the reduced catalysts forming large Cu particles in poor contact with ZnOₓ that results in a significant decrease in the intrinsic activity of the copper active sites for methanol synthesis.

Keywords: sodium; hydroxycarbonate; copper; catalyst; methanol

1. Introduction

Methanol is one of the most important chemicals used in several industries (global demand exceeds 75 million Mt, 2015) and it is also considered as a promising synthetic transportation fuel which can be produced from renewable resources [1,2]. Methanol is industrially produced from syngas mixtures (CO/CO₂/H₂) at low temperature (230–250 °C) and pressures in the range 50–100 bar over Cu/ZnO/Al₂O₃ catalysts that are considered the most efficient systems for methanol synthesis at low temperature [3–5]. With regard to the Cu/ZnO/Al₂O₃ catalysts, it is known that the presence of well dispersed copper particles in close contact with the partially reduced zinc oxide phase (Cu-ZnOₓ synergy) is decisive to obtain catalysts with high activity and stability [6,7]. Therefore, the development of large accessible Cu-ZnOₓ contacts is the main objective in the preparation of the Cu/ZnO/Al₂O₃ catalysts [8]. The synthesis method for preparing optimal Cu/ZnO/Al₂O₃ catalysts was developed in the 1960s and includes a multi-step preparation route starting from hydroxycarbonate precursors obtained by coprecipitation of metal nitrates with sodium carbonate, followed by the calcination and reduction steps to generate the active catalysts. The vast literature covering the optimization of the preparation of Cu/ZnO/Al₂O₃ catalysts established that the early stage of synthesis of the hydroxycarbonate precursors is a key step, because the meso- and nanostructure developed by the
In this way specific phases of copper-zinc hydroxycarbonates, such as zincian malachite \([\{\text{Cu,Zn}\}_2\text{CO}_3\{(\text{OH})_2\}_x\]\) or the amorphous georgeite \([\{\text{Cu}, \text{Zn}\}_2\text{CO}_3\{(\text{OH})_2\}_x]\) are suitable precursors \([10–12]\) because these hydroxycarbonates assure the proper meso- and nanostructure of the catalysts after the calcination and reduction steps. The insertion of Zn into zincian malachite structure favours the nanostructure (high copper dispersion in close contact with Zn) while the amorphous zincian georgeite hydroxycarbonate is responsible of the maintenance of the mesostructure of the catalysts after the calcination. This is because a part of the carbonate structure is retained after calcination (high temperature carbonates, HT-CO\(_3\)) which allows achieving high CuO and ZnO interdispersion \([11–13]\). Therefore, the synthesis of the Cu/ZnO/Al\(_2\)O\(_3\) catalysts needs careful control of the preparation parameters during the hydroxycarbonate formation, such as pH, concentration, temperature and ageing time \([9–13]\). The amount of Na\(^+\) and NO\(_3\)\(^-\) remaining in the hydroxycarbonate precipitates should be controlled because, as is well documented in the literature \([10,13–21]\), its presence inhibits the interaction and synergetic effect between Cu and ZnOx in the final catalyst leading to low copper metal surface area and catalytic activity. Therefore, in the conventional catalyst preparation by coprecipitation the effective removal of residual Na\(^+\) and NO\(_3\)\(^-\) is required by repeated washing of the hydroxycarbonate precipitates. In spite of the strong effects of Na\(^+\) and NO\(_3\)\(^-\) on the structure and activity of the Cu/ZnO catalysts, there is still discussion about how these species are involved in the modification of the meso- and nanostructure of the catalysts after the calcination and reduction steps. In fact, it is not yet clear if the negative effects are caused by the Na\(^+\) or NO\(_3\)\(^-\) ions and, therefore, different hypotheses to explain the role of Na\(^+\) and NO\(_3\)\(^-\) have been proposed in the literature \([8,13,15–21]\). Some studies have shown an increase in the size of CuO and ZnO after calcination of hydroxycarbonates and subsequent reduction because the presence of NaNO\(_3\) promotes severe metal agglomeration produced by its exothermic decomposition \([13,16,17,19,20]\). Other studies proposed that the presence of residual Na\(^+\) produces an inhibitory effect on the substitution of Cu\(^{2+}\) by Zn\(^{2+}\) in the malachite precursors, thus decreasing the number of Cu-ZnOx contacts in the final catalysts \([15,18]\). It is also proposed that high sodium content produces uncontrolled ageing leading to hydroxycarbonates of low surface area \([8]\). Other proposals indicated that the sodium ions act directly as a poison increasing the surface basicity, by blocking the active copper site sites or by inducing phase separation between the copper and Zn species \([21]\). Therefore, although the effects of Na\(^+\) and/or NO\(_3\)\(^-\) are well documented in the literature, the mechanism of modification has not yet been elucidated, in part because the effects have been individually studied on calcination or reduction steps but without evaluating the effect on the entire sequence of steps that configure the meso- and nanostructure of the Cu/ZnO/Al\(_2\)O\(_3\) catalysts.

In this work, therefore, we try to shed some light on the fundamental understanding about the effect of NaNO\(_3\) on each of the steps (calcination and reduction) involved in the formation and configuration of active sites on the Cu/ZnO-Al\(_2\)O\(_3\) catalysts and its relationship with the activity for methanol synthesis from syngas. Evolution of the hydroxycarbonate precursors with different amounts of NaNO\(_3\) was studied in deep during calcination and reduction in order to analyse the influence of the Na\(^+\) and/or NO\(_3\)\(^-\) ions on the meso- and nanostructure of the final Cu/ZnO/Al\(_2\)O\(_3\) catalysts.

2. Results and Discussion

2.1. Characterization of Precursors, Calcined and Reduced Catalysts

The amount of sodium in the hydroxycarbonate precursors subjected to the different washing cycles (W/O = precursor without washing and W1, W3 and W3 = precursors after 1, 3 and 6 washing cycles respectively, see materials and methods section) was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Table 1). The amount of sodium in the precipitates without washing was high (7.3 wt\%) because it remains strongly adsorbed on the surface of the hydroxycarbonates. This is expected taking into account its role during the crystallization of malachite.
from georgeite [13]. Considering that the sodium species adsorbed on the hydroxycarbonates are in dynamic equilibrium with the Na ions in the washing solutions its value decreases with the number of washings (Table 1). The loss of Cu and Zn ions in the successive washings was also determined in all cases to be very small (<0.1 wt%). Under our washing conditions, the Na content achieves a minimum value (0.01 wt%) after the third washing cycle.

### Table 1. Nomenclature, Na content (inductively coupled plasma atomic emission spectroscopy (ICP-EAS)) and textural properties (form N2 isotherms) of the hydroxycarbonate precursors.

| Sample | Washing (mL H2O/g)/Time (min) | Na/NaNO3 (wt %) | S_BET (m²·g⁻¹) | V_pore (cm³·g⁻¹) |
|--------|-----------------------------|----------------|----------------|-----------------|
| W/O    | 00                          | 7.339.4        | 107            | 0.461           |
| W1     | 1005                        | 0.010.05       | 128            | 0.558           |
| W3     | 30,015                      | 0.010.05       | 128            | 0.578           |
| W6     | 60,030                      | 0.010.05       | 127            | 0.579           |

* per g of hydroxycarbonate

The hydroxycarbonate precursors were studied by X-ray diffraction (XRD, Figure 1) in order to analyse the possible changes in their structure after the different washing cycles. The XRD patterns of all samples showed (Figure 1A) diffraction peaks at 2θ = 14.5°, 17.5°, 24.1°, 32.5° and 35.6° corresponding to the (2 0 2), (1 2 0), (2 2 0), (2 0 1) and (2 1 −1) crystal planes of the zinzian malachite structure (Joint Committee on Powder Diffraction Standards, JCPDS, no. 17-0216, (Cu/Zn)₂CO₃(OH)₂). The diffraction peaks of the zinzian malachite structures are of similar definition and intensity in all precipitates indicating similar crystallinity and size.

**Figure 1.** X-ray diffraction (XRD) patterns (A) and expansion in the interval 30–35° (B) of the hydroxycarbonate precursors: (a) W/O (−), (b) W1 (−), (c) W3 (−) (+ zinzian-malachite ((Cu/Zn)₂CO₃(OH)₂, * NaNO₃)).

The crystalline domain size of the malachite phase calculated from the (2 2 0) plane revealed less than 0.5% of variation in size in all samples after the different washing cycles (Figure 1B). The position of the (2 1 −1) diffraction peak is the same in all precipitates (Figure 1B) suggesting similar Zn insertion in the malachite structure since the position of this reflection is sensitive to changes in the Zn incorporation into the zinzian malachite-phase. Therefore, the XRD results seem to indicate that there is no major modification in the crystalline structure of the zinzian malachite phases of the precursors after the washing cycles. The unwashed precipitate (W/0) presented additional strong diffraction peaks at
20° 29.4°, 31.9°, 38.9°, 42.7° and 48.0° corresponding to the (1 0 4), (0 0 6), (1 1 3), (2 0 2), and (0 1 8) crystalline planes of NaNO₃ (JCPDS no. 36-1474 Figure 1A). However, the presence of crystalline NaNO₃ was not detected in any of the washed precipitates (W1, W3) as consequence of the low content of NaNO₃ in the W3 precursor (0.05 wt%) or the high dispersion of NaNO₃ in the W1 precursor that produces small crystallites of NaNO₃ not detectable by XRD (dp < 4 nm).

The absence of diffraction peaks corresponding to NaNO₃ in the W1 precursor indicated the absence of crystallites of NaNO₃ detectable through XRD (dp > 2 nm). Obviously the existence of NaNO₃ in W1 precursor was confirmed by chemical analysis and, therefore, the absence of diffraction peaks in the W1 precursor indicates the high dispersion of the NaNO₃ that produce small crystallites of NaNO₃ (dp < 4 nm) not detectable by XRD.

The structure and morphology of the precursors were analyzed by scanning electron microscopy (SEM, Figure 2). SEM micrographs of all precursors show a similar morphology composed by globular particles in combination with distorted rod-like structures. The observed structuration of the precursors is characteristic of the presence of small crystalline zincian malachite (rod like shape) [11] derived from amorphous georgeite (globular shape) [10] in line with the previous XRD patterns which revealed the existence of small crystalline domains of zincian malachite in all precursors. It is well known that the initial structure of precursors with formation of small crystals of zincian malachite is a prerequisite for the formation of porous mesostructures with a highly accessible surface area [11].

![Figure 2. Scanning electron microscope (SEM) micrographs of the hydroxycarbonate precursors (a) W/O, (b) W1, (c) W3 with two magnifications: (1), ×50,000, and (2), ×100,000.](image)

Textural properties of the hydroxycarbonate precursors were derived from N₂ isotherms (Figure S1) and the results are summarized in Table 1. All precipitates presented type IV isotherms with an H₂ hysteresis loop (Figure S1) that are characteristic of mesoporous materials with disordered porous structure. Brunauer–Emmett–Teller (BET) surface area and pore volume of the precursors show differences between the unwashed and washed samples (from 107 in the unwashed precipitate to 126–128 m²·g⁻¹ in washed samples, Table 1) despite the fact that they have similar development of...
zincian malachite phase (XRD, Figure 1) which, as indicated above, are responsible of the porous mesostructure of the hydroxycarbonate precursors. This result seems to indicate that some of the NaNO$_3$ in the unwashed precipitate partially blocks the porous structure developed by the zincian malachite in the precipitates which is opened after the removal of NaNO$_3$ by washing. In line with this, the BET surface area of precursors does not change significantly after the first washing because most of the NaNO$_3$ was removed during this first washing cycle (Table 1). However the average pore volume of the precipitates slightly increases after the first washing cycle because the successive washing cycles remove the last traces of the NaNO$_3$ inside the pores.

The thermal decomposition of precursors was studied by thermogravimetry (Figure 3A) and analysis of the evolved gases during the decomposition was followed by mass spectrometry (Figure 3B). The overall mass loss of all precursors are close to the expected value (29%) corresponding to the evolution of structural hydroxyl groups and carbonate units from zincian malachite ($\text{Cu/Zn}_2\text{CO}_3\text{(OH)}_2$). In the case of the unwashed sample an additional mass loss step was observed at $T > 650$ °C associated with the thermal decomposition of the large amount of NaNO$_3$ [22] present in this sample. The decomposition patterns of the precipitates show distinct mass loss profiles depending on the NaNO$_3$ content after the washing cycles.

![Figure 3](image.png)

**Figure 3.** Thermogravimetry/differential thermal analysis (TG/DTA) patterns (A) and mass spectrometry (MS) traces ($\text{H}_2\text{O}$ and $\text{CO}_2$) (B) corresponding to the decomposition of the hydroxycarbonate precursors: (a) W/O (−), (b) W1 (−), (c) W3 (−).
The unwashed precipitate (W/O) shows two decomposition steps at low (150–275 °C) and high temperature (600 °C) that correspond to the dehydroxylation and decarbonation of the zinzian malachite hydroxicarbonate in one step (step a 150–275 °C) while the step at high temperature is associated with the decomposition of the large amount of NaNO₃ present in this sample. In the case of the W1 precursor it decomposes in two steps at low (150–365 °C) and high temperature (365–520 °C). The decomposition step at low temperature corresponds to the dehydroxylation and partial decarbonation of the zinzian malachite hydroxicarbonate while the second decomposition step at high temperature was associated to the decarbonation of anion-modified mixed metal oxides [23] or a mixture of carbonates and oxides [24] formed from the previous decomposition step. The W3 precursor also shows the decomposition step at low temperature (150–410 °C) that correspond to the dehydroxylation and partial decarbonation of the zinzian malachite hydroxicarbonate while the second decomposition step associated to the decarbonation of the mixture of carbonates and oxides formed from the previous decomposition step shift in this case to higher temperature (410–598 °C, HT-CO₃). The origin of the decarbonation step at high temperature (HT-CO₃) was not clearly defined in the literature but it has beneficial effect for obtaining highly active catalyst since the residual carbonates after calcination produce good contact and interdispersion of CuO and ZnO leading to high Cu-ZnO synergy in the reduced catalyst [25].

The second decarbonation step of the hydroxicarbonate precursors shifts to lower temperature as the NaNO₃ content in the hydroxicarbonate precursors increases, as shown in Figure 3.

In order to investigate the role of the NaNO₃ in the decarbonation step of the hydroxicarbonate precursors, an additional thermogravimetric (TG) experiment was carried out in which the decomposition of the precursor with minimum NaNO₃ content (after three washing cycles, W3) was mixed (by grinding) with different amounts of NaNO₃ (1.8 and 5.0 wt%). The CO₂ evolved during decomposition of the W3 precursor mixed with different amounts of NaNO₃ as shown in Figure 4. The data in Figure 4 clearly show that NaNO₃ facilitates the decarbonation of the hydroxicarbonate by shifting the second decarbonation step (HT-CO₃) to lower temperature. Additional TG decomposition experiments on the W3 precipitate mixed with other Na⁺ and NO₃⁻ salts (NaCl and KNO₃) were performed in order to distinguish the effect of the Na⁺ or NO₃⁻ in the decomposition of the high-temperature decarbonation step (HT-CO₃). These results (Table S1) demonstrated that decarbonation of HT-CO₃ in precipitates is facilitated by the presence of alkali metal nitrates such as NaNO₃ or KNO₃ and not by the other NaCl salt. To the best of our knowledge, the effect of NaNO₃ on the decarbonation of HT-CO₃ during the thermal decomposition of Cu/Zn hydroxycarbonates was only suggested by Bems et al. [26] and it is demonstrated for the first time in this work. This effect may be related to the ability of the alkali metal nitrates to accelerate the decarbonation as already demonstrated in the decomposition of magnesium carbonate and hydroxycarbonates in the presence of NaNO₃ [27,28]. Few mechanisms have proposed in the literature an explanation for the effect of NaNO₃ on decarbonation, but in all of them the molten NaNO₃ facilitates the decarbonation, providing a liquid channel that promotes both the release of CO₂ and the oxide crystallization from the carbonates [29,30]. A similar mechanism could, therefore, be proposed in our case to justify the decarbonation at lower temperature by the presence of NaNO₃ observed in the Cu/Zn hydroxy carbonate precursors.

According to the TGA profile (Figure 3), the W/O, W1 and W3 precursors were calcined at 260, 310 and 360 °C, respectively, to decompose the hydroxycarbonates and to form the copper and zinc oxides in the calcined catalysts. The XRD profiles of calcined CuO/ZnO-Al catalysts (Figure 5) clearly show the impact of the residual NaNO₃ on the crystallization of the copper and zinc oxides after the decomposition of the precursors. The calcined catalyst derived from the precursor with minimum NaNO₃ content (CuO/ZnO-Al-W3) shows broad and poorly defined diffraction peaks of ZnO (JCPDS: 43-002) without any detectable peaks corresponding to CuO (JCPDS: 1-117) that demonstrated the absence of crystallization of CuO and the good interdispersion with ZnO. On the contrary, a significant increase in the segregation and crystallization of CuO and ZnO was observed on the calcined catalysts derived from precursors with residual NaNO₃. The size of CuO crystallites in the calcined catalysts increases (Table 2) as the NaNO₃ content in the precursors from which they derive increases (Table 1).
Going from the calcined catalyst derived from the unwashed precursor (CuO/ZnO-Al-W/O) to the catalyst derived from the precursor after three washing cycles (CuO/ZnO-Al-W3), the CuO crystallite size decreases from 9 nm to a value lower than 2 nm (Table 2).

Figure 4. MS CO$_2$ traces corresponding to decomposition of W3 hydroxycarbonate precursor mixed with different amount of NaNO$_3$ (a) +5.0 wt% NaNO$_3$ (−) (b) +1.8 wt% NaNO$_3$ (−), (c) as original, no NaNO$_3$ added (−).

Figure 5. XRD profiles of calcined catalysts derived from hydroxycarbonate precursors: (a) CuO/ZnO-Al-W/O (−), (b) CuO/ZnO-Al-W1 (−), (c) CuO/ZnO-Al-W3 (−) (o CuO, + ZnO, * NaNO$_3$).
Table 2. CuO crystallite size (XRD), carbonate retention (thermogravimetric analysis (TGA)), surface area and reduction temperature (from temperature programmed reduction, TPR) of calcined catalysts.

| Catalyst          | d_p CuO (nm) | HT-CO$_3$ T (°C)-wt% | S$_{BET}$ (a) (m$^2$/g) | TPR T (°C) |
|-------------------|--------------|-----------------------|--------------------------|------------|
| CuO/ZnO-Al-W/O    | 9            | -                     | 67.1                     | 265        |
| CuO/ZnO-Al W1     | 5            | 386-2.6               | 87.5                     | 195        |
| CuO/ZnO-Al W3     | <2           | 528-8.5               | 107                      | 165        |

(a) per g of CuO/ZnO-Al.

Other studies in the literature have already shown the adverse effect of NaNO$_3$ on the CuO and ZnO after calcination of hydroxycarbonate precursors but there is limited understanding of the effect of NaNO$_3$ on the growth of the Cu and Zn oxides during the calcination [17,26]. It is well known that the presence of residual carbonates after decomposition of the precursors is beneficial to obtain small CuO and ZnO particles finely interdispersed in the calcined catalysts [23–25]. The role of the residual carbonates on the dispersion of the oxide particles is still unclear but it is suggested that they serve as growth inhibitors for the oxide crystallites or that they act as binders that separates the oxide particles [25]. In line with this, the carbonate retention on calcined CuO/ZnO-Al catalysts determined by TGA (Table 2) shows a clear parallelism between the residual carbonates after calcination and the growth of CuO and ZnO on the calcined catalysts. The residual carbonates on calcined catalysts related to the decarbonation step at high temperature of the precursors (HT-CO$_3$) so that the precursors with HT-CO$_3$ will give rise to residual carbonates on calcined catalysts that inhibit the CuO and ZnO oxide growth. The CO$_2$ evolved during the decomposition of precursors (Figures 3 and 4) clearly shows that NaNO$_3$ facilitates the decarbonation of the precursors, shifting the decomposition of the HT-CO$_3$ to lower temperature. The ability of NaNO$_3$ to facilitate the decarbonation is probably related with the fact that molten NaNO$_3$ provides a liquid channel that promotes the release of CO$_2$ from the precursors [29,30]. Therefore the crystalline growth of CuO and ZnO in calcined catalysts derived from precursors with NaNO$_3$ could be due to the loss of the residual carbonates that act as inhibitors/binders as consequence of the ability of NaNO$_3$ to accelerate the decarbonation of the HT-CO$_3$ in the precursors. In addition to that, the growth of CuO/ZnO could also be related with the ability of the molten NaNO$_3$ to promote the rapid crystallization of metal oxides, as was already described in the case of MgO which shows higher crystallinity and size after decarbonation of magnesium carbonate and hydroxycarbonate in contact with NaNO$_3$ [29].

The observed differences in the thermal decomposition of precursors obviously influence on the mesostructure of the formed calcined catalysts. The calcined catalyst derived from the W3 precursor shows a surface BET area (CuO/ZnO-Al-W3 = 107 m$^2$/g$^{-1}$, Table 2) similar to the area developed by the precursor (W3 = 128 m$^2$/g$^{-1}$, Table 1). By contrast, the calcined catalysts derived from the W/O and W1 precursors show a significant loss in their BET surface area (CuO/ZnO-Al-W/O = 67.1 m$^2$/g$^{-1}$, CuO/ZnO-Al-W-1 = 87.5 m$^2$/g$^{-1}$, Table 2) respect to that developed by their precursors (W/O = 107 m$^2$/g$^{-1}$; W1 = 128 m$^2$/g$^{-1}$ Table 1). Therefore the calcined catalysts formed after decomposition of precursors develop less mesostructure and surface area as the NaNO$_3$ content in the precursors increases. It has been widely reported in the literature [31–33] that the carbonate retention after calcination determines the mesostructure of calcined catalysts because as discussed above, they inhibit the macro-crystalline growth of CuO/ZnO avoiding its macro-phase segregated agglomeration. Therefore, the results of this work illustrate that the presence of NaNO$_3$ modifies the mesostructure of the calcined catalysts because it enhances the decomposition of HT-CO$_3$ during calcination which produces macro-crystalline CuO/ZnO agglomerates with loss of mesostructure and surface area. The decomposition of HT-CO$_3$ during calcination depends on the NaNO$_3$ content as demonstrated in Figure 4 and, therefore, the growth of CuO/ZnO and loss of surface area in calcined catalysts decreases as the nitrate content in precursor increases.
The reducibility of the calcined catalysts was investigated by temperature programmed reduction (Figure 6). The temperature programmed reduction (TPR) profile of the catalyst with minimum nitrate content (CuO/ZnO-Al-W3) shows a sharp reduction peak at 165 °C preceded by a small shoulder at lower temperature. According to the general interpretation, the main reduction peak is typical of the reduction of small CuO nanoparticles highly dispersed in contact with ZnO [34,35] while the shoulder at low temperature is probably related to the reduction of finely dispersed CuO [36] or to the remaining carbonate species [37]. The latter option seems more likely because the gas analysis by mass spectrometry detected the reduction with simultaneous formation of CO₂. The calcined catalysts derived from precursors with residual nitrate (CuO/ZnO-Al-W/O and CuO/ZnO-Al-W1) show lower reducibility as consequence of their crystalline CuO and ZnO growth. The reduction temperature on these samples shifts to higher values as the dispersed CuO nanoparticles in contact with ZnO decreases in accordance with the growth and segregation observed by XRD (Figure 5). In the case of the catalyst with the highest nitrate content (CuO/ZnO-Al-W/O, Figure 6c) its reduction starts at 265 °C, which is close to that reported for bulk CuO particles. The reduction peak includes an additional sharp peak at 330 °C that corresponds to the reduction of the NaNO₃, corroborated by the NH₃ formation observed by mass spectrometry. The reduction of NaNO₃ is produced by the spillover of hydrogen on the reduced metallic copper atoms [38].

Since the size of the CuO crystallites and its interaction with ZnO particles in the calcined catalysts define the reducibility and the corresponding size of Cu⁰ nanoparticles, the nanostructure of the reduced catalysts was studied by transmission electron microscopy (TEM, Figure 7) and N₂O chemisorption (Table 3).

The reduced catalyst derived from precursor with minimum nitrate content (Cu/ZnO-Al-W3) shows aggregates of small particles formed by metallic copper with an average size of 7–8 nm homogeneously distributed and in close contact, partially covered, with ZnO (Figure 7c) forming the typical nanostructuration observed for highly active methanol synthesis catalysts [39]. By contrast, the

![Figure 6. Temperature programmed reduction profiles of calcined catalysts: (a) CuO/ZnO-Al-W/O (--), (b) CuO/ZnO-Al-W1 (--), (c) CuO/ZnO-Al-W3 (--).](image-url)
reduced catalysts derived from precursors with residual nitrate (Figure 7a,b) show higher metallic copper nanoparticles (9–10 nm for Cu/ZnO-Al-W1 and 20 nm for Cu/ZnO-Al-W/O) segregated from large ZnO particles in accordance with the growth of CuO and ZnO observed in their calcined precursors. However, the growth and segregation of metallic copper particles is especially significant in the case of the sample with the higher NaNO₃ content (Cu/ZnO-Al-W/O) and points out that in addition to the growth of CuO crystallites in the calcined catalyst, the local exothermicity generated by the reduction of the residual nitrate (Figure 6a) could also facilitate the migration and coalescence of the copper particles during reduction resulting in the observed strong Cu growth [40]. Obviously the Cu-ZnO synergy on reduced catalysts is affected by the above commented changes in the nanostructuration of metallic Cu and ZnO observed by TEM.

![Image](https://via.placeholder.com/150)

**Figure 7.** Transmission electron microscopy (TEM) micrographs of reduced catalysts: (a1,a2) Cu/ZnO-Al-W/O, (b1,b2) Cu/ZnO-Al-W1, (c1,c2) Cu/ZnO-Al-W3.

| Catalyst         | Effective Cu Surface Area (m²·g⁻¹) | Initial CH₃OH Time Yield a (µmol min⁻¹·g⁻¹) | TOF b (s⁻¹) | Deactivation Rate (µmol min⁻¹·g⁻¹) |
|------------------|-----------------------------------|-------------------------------------------|--------------|-----------------------------------|
| Cu/ZnO-Al W/O    | 0                                 | 0                                         | -            | -                                 |
| Cu/ZnO-Al W1     | 29.1                              | 300                                       | 7.0          | 0.05                              |
| Cu/ZnO-Al W3     | 41.3                              | 1050                                      | 17.3         | 0.01                              |

a initial activity at t = 0.5 h; b TOF = µmol CH₃OH/µmol Cu(surface)⁻¹·s⁻¹.

The Cu-ZnO synergy were determined by N₂O chemisorption because in addition to the measurement of the copper surface area, the N₂O chemisorption also tritates the contacts with defective ZnO₈ species [41]. Therefore, the Cu-ZnO synergy determined from N₂O chemisorption can
be used as a rough indicator for methanol synthesis activity. The N₂O chemisorption data on reduced catalysts (Table 3) show differences in accordance with the copper dispersion and contacts of the Cu nanoparticles with ZnO/ZnOₓ species previously observed by TEM. Thus the reduced catalyst derived from the precursor with low nitrate content (Cu/ZnO-Al-W3) shows a very high value of specific Cu surface area (41.3 m²·g⁻¹) in line with the small Cu nanoparticles in close contact with ZnO shown in their TEM images (Figure 7(c.2)). By contrast, the catalysts derived from precursors with residual nitrate (CuO/ZnO-Al-W/O and CuO/ZnO-Al-W1) show lower values of specific Cu surface area in accordance with the growth and segregation of the copper species observed on the TEM images of the samples (Figure 7(a.2,b.2)). It should be noted that the catalyst derived from the high-nitrate precursor (Cu/ZnO-Al-W/O) does not show any N₂O chemisorption capacity that means small copper surface area and absence of Cu-ZnO synergy. This fact is a consequence of the formation of large Cu crystallites segregated from the ZnO particles existing in this sample and derived from the macro-crystalline growth of CuO and ZnO after calcination and the strong Cu growth after reduction produced by the local exothermicity generated by the reduction of the residual nitrate.

2.2. Activity in Methanol Synthesis

The catalysts were tested in the synthesis of methanol from syngas and the activity data were presented in Figure 8 and collected in Table 3. As expected, the changes observed in the nanostructure, crystallization and segregation of Cu and ZnO in the reduced catalysts caused by the NaNO₃ in precipitates produce very significant changes in their activity for methanol synthesis. The catalyst derived from the precipitate without washing (with maximum NaNO₃ content, Cu/ZnO-Al-W/O) was ineffective for methanol synthesis. This behaviour could be correlated with the small copper surface area and absence of Cu-ZnO synergy (Table 3) derived from the large Cu crystallites with poor contacts with ZnO observed in this reduced catalyst (Figure 7(a.2)). The methanol activity of catalysts derived from washed precursors (Cu/ZnO-Al W1 and Cu/ZnO-Al W3) increase with decreasing residual NaNO₃ content in the samples, displaying the catalyst with minimum nitrate content (Cu/ZnO-Al W3) a very high performance in methanol synthesis (1050 μmolCH₃OH min⁻¹·g⁻¹-cat) that decreases by more than a third in the case of the sample Cu/ZnO-Al W1 (300 μmolCH₃OH min⁻¹·g⁻¹-cat). Higher stability is also observed for the Cu/ZnO-Al W3 that show a more stable methanol production compared to the slight decay observed for the Cu/ZnO-Al W1 sample with residual sodium nitrate (Table 3).

![Figure 8. Activity measurements in methanol synthesis from syngas vs. time on stream (TOS) (250 °C, P = 3 MPa, GHSV (gas hourly space velocity) = 32,700 h⁻¹) over: (●) Cu/ZnO-Al-W/O, (▲) Cu/ZnO-Al-W1, (■) Cu/ZnO-Al-W3.](image)
It is well known that the activity of methanol synthesis within families of Cu-ZnO catalysts prepared by the same methodology is correlated with the copper surface area and Cu-ZnO synergy determined by \( \text{N}_2\text{O} \) chemisorption. However, the intrinsic activity of catalysts calculated with respect to Cu surface areas (TOF in Table 3) shows an important difference between the samples derived from washed precursors with different NaNO$_3$ content, dropping by more than half in the case of the Cu/ZnO-Al W1 catalyst (7.0 s$^{-1}$) respect to the catalyst with the lowest nitrate content Cu/ZnO-Al W3 (17.3 s$^{-1}$).

As indicated previously the activity of copper catalysts strongly depends on the Cu-ZnO synergy that defines the nature of the active site which, although still under debate, is related to the close contact of Cu and reduced ZnO species: Cu$^{0}$–Zn$^{0}$ surface alloy [42], Zn$^{8+}$ species at the defective Cu$^{0}$ surface [8] or graphitic-like ZnO$_x$ layer on Cu$^{0}$ [43]. Therefore, the difference in the intrinsic activities observed between the washed Cu/ZnO-Al-W1 and Cu/ZnO-Al W3 catalysts is a clear indication of the change in the nature of the active sites in the sample derived from precursors containing NaNO$_3$. Regardless of the active site model, to obtain high active sites in Cu-ZnO-Al catalysts it is necessary to start from mesostructured calcined catalysts which contain finely interdispersed CuO and ZnO nanoparticles with improved reducibility that facilitates the formation, after reduction, of small Cu nanoparticles homogeneously distributed and in intimate contact with partially reduced ZnO$_x$ entities (strong metal-support interaction). This is the case of the calcined precursor derived from the precipitate with low nitrate content (Cu/ZnO-Al W3) that displays small CuO nanoparticles highly dispersed in contact with ZnO (Figure 5c) mesostructured and stabilized by residual carbonates that allows the reduction at low temperature with the formation of small Cu particles in close contact with ZnO (ZnO$_x$) nanoparticles (Figure 7(c1,c.2)). By contrast, the significant increase in the segregation and crystallization of CuO and ZnO produced by the decomposition of HT-CO$_3$ promoted by the presence of NaNO$_3$ in the calcined CuO/ZnO-Al-Al W1 precursor (Figure 5b) leads to lower reducibility and larger Cu particles with poorer contact with ZnO (Figure 7(b1,b.2)) which explains the lower intrinsic activity of the active sites of this catalyst by loss of the nanostructuration in the contact of Cu with the reduced ZnO species.

Summarizing, the results presented in this work shows that residual NaNO$_3$ on precipitates first produces the loss of the mesostructuration in the calcined catalysts. The modification in the mesostructuration of the calcined catalysts depends on the NaNO$_3$ content and it affects their subsequent evolution after reduction producing large Cu particles in poor contact with ZnO$_x$ which translates into active sites with poor intrinsic activity. The loss of the mesostructuration in the calcined catalysts was investigated in detail and it was demonstrated for the first time that is related with the decarbonation of the hydroxycarbonates at low temperature mediated by the presence of NaNO$_3$.

3. Materials and Methods

3.1. Catalysts’ Preparation

The hydroxycarbonate precursors were prepared by co-precipitation of Cu$^{2+}$/Zn$^{2+}$/Al$^{3+}$ ions using the optimized coprecipitation method developed by Schuman et al. to obtain highly active catalysts [44]. The atomic composition of the precursors (68:29:3 Cu:Zn:Al) was chosen to achieve the optimal incorporation of Zn into the Cu-malachite hydroxycarbonate precursor with the maximum promoting effect of the Al-dopant [45]. The hydroxycarbonate precursor was precipitated at constant pH (6.5) and temperature (65 °C) under continuous stirring using 1 M solutions of the nitrate salts of Cu (Cu(NO$_3$)$_2$·2.5H$_2$O, Sigma-Aldrich >98%), Zn (Zn(NO$_3$)$_2$·6H$_2$O, Sigma-Aldrich >99%), and Al (Al(NO$_3$)$_2$·9H$_2$O, Sigma-Aldrich >99%) and 1.6 M solution of sodium carbonate (Na$_2$CO$_3$·8H$_2$O, Panreac AppliChem for Analysis) as precipitating agent. The initial precipitate was amorphous in the form of georgeite. However, after 30 min of aging, there was a decrease in pH related to the transformation of the amorphous georgeite into the crystalline malachite [9]. This transformation was associated with a change in the colour of the precipitates from the blue of the georgeite to the greenish
of the malachite. Once the change in colour occurred, the precipitate was additionally aged for another 15 min to assure the complete crystallization of the malachite precipitate. The aged precipitate was filtered to separate the precipitate from the mother liquor. An aliquot of the precipitate was isolated as a sample without washing treatment (W/O sample). The rest of the precipitate was washed under stirring (500 rpm) with miliQ water (100 mL/gprecipitate) for 5 min. The solid was filtered after this first washing treatment and an aliquot of the washed solid was isolated (W1 sample). The rest of the precipitate was subjected to five additional washing cycles under stirring (500 rpm) with miliQ water (100 mL/gprecipitate for 5 min) and taking samples after 3 (W3 sample) and 6 (W6 sample) washing cycles. After washing, the precipitates were dried at 70 °C for 12 h. Table 1 shows the nomenclature and characteristics of the precipitates subjected to different washing cycles used in this study. Dried hydroxy carbonate precursors were calcined under static air for 2 h (heating rate of 2 °C·min⁻¹) to maintain in each calcined catalyst the optimal quantity of residual high temperature carbonates (HT-CO₃). According to the TGA profile (Figure 3), the W/O, W1 and W3 precursors were calcined at 260, 310 and 360 °C, respectively, to decompose the hydroxycarbonates and to form the copper and zinc oxides in the calcined catalysts. Calcined samples were reduced in order to obtain the Cu/ZnO-Al₂O₃ catalysts in their activated form. The activation consists in a thermal treatment under H₂/Ar flow (2.2 vol. %, 50 mL·min⁻¹) following the temperature program: RT→(2 °C·min⁻¹)→150 °C→(1 °C·min⁻¹)→200 °C (2 h).

3.2. Catalysts Characterization

The Na content on hydroxy carbonate precursors was determined by ICP-AES in an ICP-AES Optima 3300 DV Perkin Elmer spectrometer with an Echelle net combined with SC (scintillation counter) detectors.

The crystalline structure of the hydroxy carbonate precursors, calcined and reduced catalysts were determined by XRD using a polycrystal X-ray diffractometer XPert Pro with X’Celerator detector from PANalytical (Malvern, Worce, UK). Each sample was measured in quantitative mode using CuKα radiation (λ = 1.5406 Å, 45 kV and 40 mA), with a 0.04 step size and an accumulation time of 50 s/step. Identification of the phases was achieved by comparison with the JCPDS diffraction data file. Zinc malachite and CuO average crystal sizes were calculated from the characteristic reflection peaks of the (2 2 0) and (1 1 1) planes, respectively, using the Debye-Scherrer equation.

Textural properties of the hydroxy carbonate precursors and calcined catalysts were obtained from the N₂ adsorption/desorption isotherms measured at −196 °C. The measurements were carried out in automatic ASAP 2420 equipment (Micromeritics, Norcross, GA, USA) after the degassing of the samples at 120 °C for 12 h. The specific surface area (S BET) was calculated by the Brunauer–Emmett–Teller (BET) method. The pore volume (V pore) and the average pore size distribution (Dpore) were calculated from desorption data by the Barrett–Joyner–Halenda (BJH) method.

Thermo-gravimetric analysis (TGA) was used to determine the weight loss of the precipitates and calcined catalysts during their thermal treatment in air. The TGA experiments were carried out in a TGA/SDTA 851e balance (Mettler Toledo, Columbus, OH, USA). Samples were placed into an Al-ceramic reactor under 25 mL/min of a 20 vol.% O₂/N₂ gas flow and heated from 40 °C to 600 °C at 10 °C/min heating rate. Analysis of the evolved gases during the thermal treatment of the precipitates in air was followed by mass spectrometry (MS). The sample (20 mg) was placed in a U-shape quartz reactor (4.0 mm ID) and heated from 40 °C up to 600 °C with heating ramp of 10 °C/min under O₂/Ar flow (20 vol. %, 38 mL/min). The evolved gases were analysed online using a Baltzer Prisma QMS 200TM mass spectrometer (Pfeiffer Vacuum, Asslar, Germany) with a quadrupole detector. The studied m/z signals (H₂O, CO, CO₂, NO, NO₂, N₂O and Ar) were normalized with respect to the Ar signal to avoid the changes in the chamber pressure. Analysis of the morphology of the particles present in the precipitates and calcined catalysts were carried out by emission scanning electron microscopy (SEM) in a FE-SEM Hitachi S-4700 cold cathode field emission microscope.

Nanomorphology of the particles in the reduced catalysts were studied by transmission and high-resolution transmission electron microscopy (TEM and HRTEM, respectively) in a TEM/STEM.
JEOL 2100F microscope (JEOL, Tokio, Japan) with a field emission gun (FEG) which operates at 200 kV of accelerating voltage.

Reducibility of the calcined catalysts was studied by hydrogen temperature programmed reduction (H2-TPR). TPR experiments were carried out in semi-automatic equipment (PID Eng and Tech, Micromeritics, Norcross, GA, USA) with a thermal conductivity detector (TCD). 30 mg of calcined sample was placed into a U-shaped quartz reactor (4.0 mm ID) and heated from 25 up to 300 °C with a heating rate of 10 °C·min⁻¹ under H2/Ar flow (10 vol.%, 50 mL·min⁻¹).

N2O chemisorption experiments on the reduced catalysts were carried out to calculate the Cu-surface area using the same equipment employed for TPR experiments. Reduced catalysts (30 mg) were treated with 7.5 mL·min⁻¹ of 2 vol.% N2O/Ar at 25 °C for 5 s. Physisorbed N2O was removed with 30 mL·min⁻¹ of He flow for 30 min. Then, the N2O passivated catalysts were re-reduced with 50 mL/min of H2/Ar (10 vol.% from 25 °C up to 280 °C (heating rate of 10 °C·min⁻¹). The amount of hydrogen consumed during the re-reduction was equivalent to the amount of N2O chemisorbed. The surface of exposed Cu is calculated from the N2O chemisorption stoichiometry (Cu/N2O = 2) and the value of 1.47·10¹⁹ at Cu/m² for the mean surface Cu atom density [46].

3.3. Catalytic Activity Tests

The catalytic methanol synthesis reaction was carried out in a stainless steel continuous flow fixed-bed reactor (8.9 mm internal diameter (ID)). Catalytic bed consisted on 200 mg of calcined catalysts diluted with SiC (1:3 vol.) to avoid temperature gradients. Calcined precursors were reduced under H2/Ar flow (2.21 vol.%, 50 mL·min⁻¹) at 200 °C for 2 h. The reactor was fed with 75 mL/min of syngas (vol.%, 4.5% CO2, 22.0% CO, 58.8% H2 and 14.7% N2) and the methanol synthesis rate was measured under a total pressure of 3 MPa at 250 °C for 8 h. The catalytic tests were conducted under high gas hourly space velocity (GHSV) to achieve low conversions to exclude the effect of equilibrium and to better visualize the differences between the samples. Analysis of reaction products was accomplished on-line by gas chromatography using a Varian 450-GC equipment with TCD and a QS-bond column (for CO2, CH3OH and H2O) and a molecular sieve 5A capillary column (for H2, O2, N2, and CO). Activity data are presented as CH3OH production rate normalized to the weight of calcined precursor loaded in the reactor (μmolCH3OH·min⁻¹·gcat⁻¹).

4. Conclusions

The effect of residual NaNO3 on hydroxycarbonate precipitates on the formation and configuration of active sites on the Cu/ZnO catalysts has been studied. Evolution of the hydroxycarbonates during calcination was studied in depth in order to analyse the effect of residual NaNO3 on the mesostructuration and CuO/ZnO interdispersion. The results show that residual NaNO3 on precipitates strongly affects their transformation into calcined catalyst destroying the mesostructuration and producing segregation and crystallization of CuO and ZnO, more pronounced as the NaNO3 content in the hydroxycarbonates increases. This fact is related to the decarbonation of the HT-carbonates facilitated by the NaNO3, which is described for the first time in this work. It is proposed that molten NaNO3 facilitates the decarbonation providing a liquid channel that promotes both the release of CO2 and the oxide crystallization from carbonates. The loss of mesostructuration in calcined catalysts affects the subsequent reduction step, decreasing the reducibility and altering the nanostructuration of the reduced catalyst forming large Cu particles in poor contact with ZnOx. The loss of meso- and nanostructuration depends on the NaNO3 content and become more pronounced as the NaNO3 content increases. In the case of high NaNO3 content, the shift in the reduction temperature is such that reduction also includes the reduction of the residual nitrate creating local exothermicity that produces the migration and coalescence of the copper particles resulting in strong Cu growth. The changes in the meso- and nanostructuration of the reduced catalysts caused by the NaNO3 produce a decrease in their activity for methanol synthesis with an absolute lack of activity in the case of the catalyst with high NaNO3 content as befits its large Cu crystallites with poor contacts with ZnO.
Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/10/11/1346/s1, Figure S1: N2 adsorption/desorption isotherms (A) and pore size distribution (B) of the hydroxycarbonate precursors: (a) W/O (−), (b) W1 (−), (c) W3 (−), (d) W6 (−), Table S1. Effect of Na+ and NO3− salts (1.8 wt%) on the decarbonation step at high temperature of the W3 hydroxycarbonate precursor.

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