Cux/ZnO-y Catalysts. Effect of Support Modification by High Energy Milling on the Metal-Support Interaction [†]

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Abstract: Commercial ZnO, was subjected to high-energy milling to introduce structural modifications, which can result in a different metal-support interaction. The milling time (0 to 960 min) and vial material and mill balls (WC and ZnO_2), were modified. The supports were characterized by XRD, Scherrer, S_{BET} and Raman Spectroscopy. With the increase in milling time, an increase in the accrued kinetic energy (E_{cum}) was observed. For the same E_{cum}, with ZrO_2, twice the area was obtained in just 6 min. Cu was deposited on both, the milled support (ZnO-z) and unmilled support (ZnO-0) in three compositions; x = 0.2, 0.5, and 1.0 (%wt). AAS measurements showed Cu compositions similar to the theoretical ones. XRD studies, Rietveld modelling and Raman Spectroscopy confirmed that Cu^{2+} cations could be localized, either by substituting the Zn^{2+} ions or interstitially in the network, depending on the metal content. The TPR profiles showed two types of copper species, which interact differently with the support. Likewise, the analysis of the XPS results showed that, with the increase in Cu content, for Cux/ZnO-0, there is a decrease in the metal-support interaction. However, for Cux/ZnO-z the interaction increases, which can be associated with the introduction of structural defects accompanied by superficial energy changes. For both systems, different catalytic behaviours are expected in the hydrogenolysis reaction of glycerol in liquid phase, regarding selectivity and stability, as a result of the metal-support interaction achieved.

Keywords: zinc oxide; copper; high energy milling; metal-support interactions

1. Introduction

The selectivity towards one or more reaction products exclusively depends on the structural characteristics and the physical-chemical surface of the catalyst used. In the glycerol hydrogenolysis reaction, the supports have a strong involvement in the selectivity towards a determined reaction product. In particular, the metal-support interaction plays a key role, although it has been less investigated. The specific surface area, the superficial structural defects such as oxygen vacancies, and the acidity-basicity are, among others, characteristics that define the use or not of a metal oxide as support. These characteristics, together with the method of deposition of the metallic precursor, define the size of metallic domains, their dispersion, and the type of interaction that can occur between them.

High energy milling is considered a novel method in the synthesis of materials. This method allows us to achieve transformations of crystalline phases, an increase in surface areas and it has even been used in the activation of precursors of different catalytic systems. Moreover, it is a very powerful technique for the synthesis of catalytic materials due to the extreme conditions of pressure and

temperature that are locally reached [1]. The Cu-ZnO catalytic system has been successfully used in the hydrogenolysis reaction of glycerol, which has been mainly associated with the dispersion of Cu with small particle sizes [2]. However, very few studies have revealed that the interfacial area between Cu and ZnO plays a crucial role in the activity and the stability of the Cu-ZnO system [3]. Unfortunately, the role of the interface between Cu and ZnO in the hydrogenolysis of glycerol has been rarely reported.

The objective of this work is to modify the ZnO structural and surface characteristics due to a high energy milling, and then, to use it as catalytic support. The aim is to study the Cu-ZnO interaction achieved when the support is milled and compare it with the same system using the unmilled support.

2. Materials and Methods

2.1. Support and Catalysts Preparation

Commercial ZnO was subjected to high energy milling in a planetary ball mill (Fritsch Pulverisette 6). Four balls (1.5 cm ø) and a vial (7.0 cm ø) of WC and 2466 balls (0.5 cm ø) and a vial (10.0 cm ø) of ZrO_2 were used. For WC, a mass of balls: mass of powder ratio (BPR) of 35:1, rotation speed of 300 rpm and milling times of 0, 5, 30, 60, 240, 480 and 960 min were used. While with ZrO_2 a BPR of 148:1 and 300 rpm were used and it was milled for 6 min. This support was named ZnO-z. Copper acetate was deposited by impregnation at incipient moisture on unmilled zinc oxide (**ZnO-0**) and milled (**ZnO-z**). Three compositions of Cu (% wt) were used. The catalytic systems were named: **Cux/ZnO-0** and **Cux/ZnO-z**, with x = 0.2, 0.5 and 1.0.

2.2. Characterization

Supports and catalysts were characterized by means of X-ray Diffraction (XRD), Brunauer-Emmet-Teller (BET) method, Raman spectroscopy, Atomic Absorption Spectroscopy (AAS), X-ray Photoelectron Spectroscopy (XPS) and Temperature Programmed Reduction (TPR).

3. Results and Discussion

Commercial ZnO with a low surface area was subjected to milling. When WC was used, an increase in accumulated kinetic energy (E_{acum}) was observed with increasing the milling time [1]. Along the same lines, the S_{BET} also increased until 60 min of milling (6.03 $m^2 g^{-1}$), decreasing later due to a process of agglomeration of the particles. To determine the effect of the use of ZrO_2 on the support, the E_{acum} of the WC at 60 min of milling was taken as a reference, and the time necessary to reach it was calculated, which was only 6 min. Milled ZnO presented a S_{BET} three times higher than that of the unmilled support (Table 1); Therefore, it was selected as a support for the Cux/ZnO-z system. In order to determine the effect of milling on the metal-support interaction, the Cux/ZnO-0 system was synthesized as a reference. The characterization of the supports is not presented due to the space limit.

XRD diffractograms are shown in Figure 1. In both systems, diffraction lines typical of the hexagonal system of wurtzite (PDF 96-90-4181) can be observed, without any diffraction lines corresponding to phases containing Cu. This may be due to its low Cu concentration, high dispersion and/or the incorporation of Cu ions in the ZnO structure. The observed shift of the most intense diffraction signal (101) of ZnO (Figure 1) indicates the incorporation of Cu into the ZnO lattice, in different extensions, in both systems. In the Cux/ZnO-0 system, the increase of the Cu content leads to a decrease in the displacement. Cu0.2/ZnO-0 shows the highest displacement, which is a sign of constant lattice contraction. This can be attributed to the internal relaxation of the lattice, due to the incorporation of Cu^{2+} ions (0.073 nm) in the bigger Zn sites (0.074 nm) [4]. For 0.5% and 1.0%, the lower displacements can be associated with a lower incorporation of Cu^{2+} in the ZnO lattice, and a favouring of the nucleation process and the subsequent growth rate of CuO, due to the higher concentration of Cu. Contrary to Cux/ZnO-z, the diffraction lines shift towards greater angles with increasing Cu content. This can be associated with the continuous migration of the Cu^{2+} species in the

ZnO matrix, occupying positions in its planar defects, whose content is higher in ZnO-z due to milling.
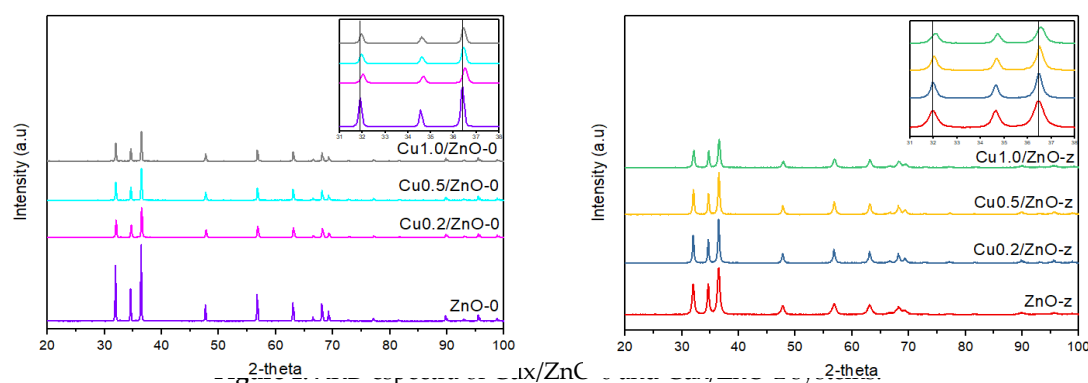
Different parameters of the ZnO crystal structure, for both systems, calculated from the XRD data, Scherrer equation and Rietveld modelling are presented in Table 1 [4]. For Cux/ZnO-0 it can be observed that the D values are lower than those with the support, which can be associated with the alteration in the host lattice, due to the insertion of Cu. However, D increases with the increase in Cu content, indicating a lower insertion of Cu^{2+} in the ZnO lattice, in line with what was observed by XRD. The ZnO-z support has a D lower than ZnO-0, as a consequence of the milling. In Cux/ZnO-z, an increase in D is observed when Cu is added, which would indicate the incorporation of Cu in the ZnO. However, D decreases when more Cu is added. Although with the increase in copper, more Cu^{2+} ions are incorporated, it is possible that they are located in positions that stabilize the ZnO-z lattice and/or part of the Cu^{2+} located in tetrahedral positions is reduced to Cu^+, which has a lower ionic radius (0.060 nm) and leads to external relaxation of the closest O atoms, contracting the crystalline lattice. It has been reported that Cu^+ ions can come from the transformation of Cu^{2+} ions that capture an extra electron from a nearby atom or in complexes with oxygen vacancies [5].

For both systems, the c/a cell parameters relationship changes concerning the supports, which indicates a structural deformation of the material [4], confirming the incorporation of Cu in it. For Cux/ZnO-0 the c/a ratio decreases, while no variations are observed when the Cu doping increases, which can be explained by a limited insertion of the cation in the support lattice, for the three catalysts. In Cux/ZnO-z, the c/a ratio is higher than that of the support and it increases with the addition of Cu, due to its continuous incorporation into the structure. The intrinsic stress (ξ) and the density of the grain boundaries (dislocations (δ)) also provide information on stresses and defects introduced in the support crystalline lattice by the incorporation of an ion and/or milling [4]. In Table 1, it can be observed that for the Cux/ZnO-0 system, the ξ and δ values increase in the support, which can be attributed to the changes in the microstructure, size, and shape of the particles, due to the Cu insertion. However, ξ and δ decrease with the increase of Cu, which would indicate that the nucleation process of the Cu excess is favoured, instead its incorporation into the structure. As expected for the support subjected to milling, ξ and δ present high values due to the great stresses and defects introduced in the lattice. In the Cux/ZnO-z system, with the addition of Cu, ξ and δ tend to decrease, which would indicate that the Cu atoms could occupy positions in the lattice, stabilizing it and releasing the stress generated by the milling. However, with the increase in Cu content, both increase due to a greater incorporation of Cu, without reaching the values obtained for ZnO-z. Therefore, it could be said that doping with Cu, in general, improves the stability of the lattice.

Raman spectroscopy corroborates what it is mentioned above. In the supports, the E2(high) no polar mode predominates at ~438 cm^{-1}, which it is characteristic of the wurtzite hexagonal phase. The intensity of this mode dramatically decreases with the milling. Also, it expands and increases its asymmetry, indicating a further disarray of the lattice. The absence of vibrational modes corresponding to the Cu oxide phases demonstrates its incorporation into the ZnO lattice and/or a high dispersion of CuO. It has been reported that the I_{E1}/I_{2A1} intensities ratio allows identifying the content of defects in a solid, in particular, the oxygen vacancy type [6]. For Cux/ZnO-0 this ratio is

higher than for the support, but it decreases with the Cu content increase. However, for Cux/ZnO-z this ratio decreases considering the support, indicating a decrease in the number of defects and the Cu content increase.

Table 1. Data obtained from XRD, Scherrer equation, Rietveld modelling, AAS and Raman spectroscopy.

Catalyst	D (nm)	c/a	$\xi \times 10^{-4}$	$\delta \times 10^{14}$ line m^{-2}	S_{BET} (m^{2}g^{-1})	Cu (%wt)	I_{E1}/I_{2A1}
ZnO-0	71.2	1.6026	15.60	1.97	3.8	-	0.18
Cu0.2/ZnO-0	44.0	1.6020	25.09	5.16	3.7	0.2	0.64
Cu0.5/ZnO-0	50.7	1.6020	22.00	3.89	3.5	0.56	0.31
Cu1.0/ZnO-0	55.8	1.6020	19.98	3.21	4.5	0.96	0.17
ZnO-z	16.8	1.6017	66.06	35.43	14.54	-	1.78
Cu0.2/ZnO-z	31.7	1.6020	35.02	9.95	6.54	0.25	1.53
Cu0.5/ZnO-z	28.6	1.6021	38.78	12.22	5.97	0.68	1.37
Cu1.0/ZnO-z	21.1	1.6023	52.52	22.46	7.5	1.19	1.04

The S_{BET} of the Cux/ZnO-0 system practically does not vary with the doping of Cu. On the contrary, in the Cux/ZnO-z system, the S_{BET} decreases with the incorporation of Cu, but increases with the increase of the Cu content. This could be associated with the impregnation stage, where the incorporated moisture and the subsequent calcination would favour the coalition of the ZnO small agglomerated particles, obtained during the milling. The impregnating solution of copper acetate with a pH = 5.5–6.0 could erode the ZnO surface, which is easily attacked by acids, explaining the slight increase in the S_{BET} with the increase in the Cu content, in both systems. The composition data, obtained by atomic absorption for both families, show excellent impregnation, since the experimental values are similar to the theoretical ones (Table 1).

XPS was used to understand the surface modifications introduced by the milling on the support, and the interaction achieved between the metal-support (Table 2). In both systems, shifts were observed in the Zn 2p1/2 and 2p3/2 signals, corresponding to ZnO [7] at higher binding energies (BE), with respect to the two supports; indicating a strong Cu-ZnO interaction. In Cux/ZnO-0 the displacement decreases with increasing Cu content, which would indicate a decrease in this interaction as more Cu is deposited. An inverse behaviour can be observed in Cux/ZnO-z, indicating a greater Cu-ZnO interaction as more metal is deposited. Cu2p1/2 and 2p3/2 signals also show shifts, but more marked for the two systems, but at lower BE than those reported in the literature for CuO (953.2 eV and 933.5 eV) [7]. This is associated with the Cu-ZnO interaction. With increasing copper content, there is no linear behaviour. According to I. Kaskow et al. [7], the increase in the BE in Zn 2p3/2, and its decrease in the supported metal, implies an electronic transfer from the support to the metal. This could induce the reduction of CuO to Cu_2O, at the interface between the metal domain and the support, in both families. The presence of a satellite signal at ~943 eV is characteristic of materials having a d9 configuration in its highest oxidation state (CuO). In Cux/ZnO-0, this satellite is almost imperceptible for 0.2%, but its intensity increases with the Cu content. For Cux/ZnO-z, it can only be observed with a very low intensity (1.0%). Although the CuO formation increases with the addition of Cu, in both systems, its content is higher in the Cux/ZnO-0 system. The O1s signal was deconvolved into two signals (Table 2). These signals correspond to oxygen of the crystalline lattice, O_{lat}, at 530.1-530.4 eV, and oxygen adsorbed in oxygen vacancies, O_{ads}, at 531.7-532.3 eV. Milling causes a shift of these signals to lower BE, which is associated with internal stresses in the lattice, and generated defects. For Cux/ZnO-0, the O_{lat} do not vary with the Cu content increase, but their signal moves to higher BE. This could be explained by the limited incorporation of the Cu in the ZnO lattice. On the contrary to O_{ads}, its BE increases with the copper content, being higher than that of the support, which could indicate a strong interaction of Cu with these defects. Indeed, this is the case, since the total content of O_{ads} decreases with the addition of Cu, which would indicate a selective

adsorption of the metal in this type of defects, in line with the variations in the ratio of intensities observed by Raman. In Cu_x/ZnO-z, the O_{lat} moves to higher BE and increases with the addition of copper. This can be associated with the constant incorporation of Cu into ZnO-z. The O_{ads} show a lower displacement at higher EB with respect to the support, but it also increases with the Cu content. In this system, copper is also selectively adsorbed on oxygen vacancies; but in a lesser degree than for the Cu_x/ZnO-0 system. If we compare the occupied O_{ads} in percentage terms, after Cu deposition, for Cu1.0/ZnO-0 it is 51%, while for Cu1.0/ZnO-z it is 30%; and at the other extreme, for Cu0.2/ZnO-z the O_{ads} are not modified by the addition of Cu, while for Cu0.2/ZnO-0 30% is occupied. These results allow us to infer that in Cu_x/ZnO-0 part of the deposited Cu is incorporated into the ZnO lattice, while the rest of it is selectively adsorbed on the oxygen vacancies, leading to a nucleation process to obtain CuO. As in Cu_x/ZnO-z, a higher percentage of Cu is incorporated into the lattice of the milled support; the rest is located in the oxygen vacancies, forming CuO. Therefore, different Cu contents with Cu^{2+} and Cu^+ valences can be expected in the two systems.

Table 2. XPS and TPR analysis of supports and catalysts.

Catalyst	O 1s (eV)		Zn 2p$_{3/2}$ (eV)	O$_{ads}$/ (O$_{ads}$+O$_{lat}$)	Cu 2p$_{3/2}$ (eV)	Reduction Temperature (°C)		H$_2$ consumption (µmol H$_2$ g^{-1} Cu)		
	O red	O ads				Signal 1	Signal 2	Exp.	CuO	Cu$_2$O
ZnO-0	530.15	531.67	1021.38	35.60	-	-	-	-	-	-
Cu0.2/ZnO-0	530.43	532.07	1021.77	24.65	932.43	218	267	26.6	31.4	17.5
Cu0.5/ZnO-0	530.40	532.30	1021.73	21.53	932.73	217	272	67.8	87.5	45.5
Cu1.0/ZnO-0	530.38	532.34	1021.58	17.44	932.31	213	262	109.5	149.6	83.2
ZnO-z	530.07	531.65	1021.28	24.30	-	-	-	-	-	-
Cu0.2/ZnO-z	530.19	531.85	1021.29	24.67	932.52	213	243	21.5	25.1	14.0
Cu0.5/ZnO-z	530.22	531.89	1021.45	22.03	932.44	200	244	42.9	70.3	39.2
Cu1.0/ZnO-z	530.38	532.19	1021.59	17.07	932.39	200	241	88.1	120.7	66.2

RTP is a bulk technique that provides information on the reducibility of the systems, the possible Cu oxidation states, and Cu-ZnO interaction. The reduction profiles of the catalysts in both systems are the same. They present two overlapped signals, which move to lower reduction temperatures with the Cu content increase; while the supports do not present reduction signals in the temperature range studied. For Cu_x/ZnO-z the copper reducibility is higher than in the other system. All the catalysts have lower Cu reduction temperatures than that corresponding to the bulk CuO reduction (347 °C), indicating a strong copper-support interaction. The two signals present in the reduction profiles have been associated with the reduction of different copper species by different authors. Gao et al. [2] associate the first signal to the reduction of highly dispersed CuO and the signal at high temperature to bulk CuO. G. Fierro et al. [8] associate them with the reduction of CuO with different interactions with ZnO, while X. Yang et al. [3] associate the signal at low temperature to the reduction of Cu^{2+} to Cu^+ and the signal at high temperature to the reduction of Cu^+ to $Cu°$. With the aim to better understand our results, the H_2 consumptions were calculated and compared with the theoretical values, corresponding to the Cu content deposited in each catalyst; for the reduction of CuO and Cu_2O (Table 2). Cu_x/ZnO-0 presents consumptions close to the theoretical ones for the exclusive reduction of CuO, but when the copper content increases, the experimental consumptions are lower than the theoretical ones, which could indicate the presence of a low amount of Cu_2O. The coexistence of copper with both valences is possible due to electronic mobility that occurs from the support to the metal, as inferred from XPS. The greater amount of Cu_2O with the increase in the copper content could be associated with highly dispersed small metallic domains, where the bulk of the metallic particle corresponds to CuO, and the metal-support contact area, which would increase with dispersion and domain size reduction, is where Cu_2O would be formed. On the contrary, Cu_x/ZnO-

z presents experimental consumptions close to the theoretical consumptions for the exclusive reduction of Cu_2O. In this case, with the increase in the copper content, the theoretical consumptions are higher than the theoretical for the exclusive reduction of Cu_2O, which would indicate the presence of a small amount of CuO. The possibility of having Cu_2O and CuO, but in an inverse relationship to that of the unmilled system, could be explained by the greater incorporation of Cu in the ZnO lattice. This facilitates its reduction, possibly due to the formation of very small metallic domains, dispersed and with a greater interaction with the support, at low bulk CuO, but increasing when more copper is added.

4. Conclusions

High energy milling generates an increase in the specific surface area of the support, and introduces defects and micro-stresses in the crystalline lattice, making it more reactive than the original crystalline structure. The vial and mill balls material has a great influence on the milling time, generating different changes in the solid for the same accumulated kinetic energy. The defects introduced in the support by the high energy milling increase the metal-support interaction, and the reducibility of the metal; and Cu insertion could be potentially stabilizing the ZnO lattice, as inferred from the techniques discussed in this work. As a consequence, it is possible a decrease in the sizes of metallic domains and an increase in their dispersion, which will soon be determined by chemisorption of N_2O. For Cux/ZnO-z, the CuO/Cu_2O-ZnO-z generated interface could lead to an improvement in the activity, selectivity and stability of this system in the glycerol hydrogenolysis reaction. We can conclude that high energy milling is an environmentally friendly technique, and very powerful. It allows modifying the metal-support interactions, which could be reflected in the improvement of the performance of catalytic systems in liquid phase reactions.

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

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