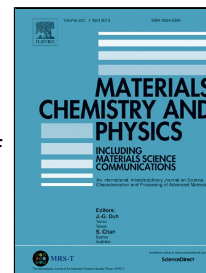


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Preparation and Characterization of Cu-CeO₂ catalytic materials for the Oxidation of Benzyl Alcohol to Benzaldehyde in Water

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ABSTRACT

A series of Cu-CeO₂ catalytic materials, with copper loadings in the 5-20 wt% range, was prepared, characterized and tested in the oxidation of benzyl alcohol to benzaldehyde in batch conditions, at 100°C employing water as the solvent. Different CeO₂ and Cu-CeO₂ samples were obtained following hydrothermal synthesis, combustion of nitrates, and impregnation of copper salts on ceria surface. The characterization of the catalysts was carried out by N₂ sorption, XRD, XPS, SEM, TEM, N₂O dissociative chemisorption and FT-IR. Ceria properties play a notable role over copper activity and selectivity for the oxidation of benzyl alcohol. The material prepared by the simple one-pot combustion method, with 18wt% of copper, showed high activity and high selectivity to the desired product (90% at 40% of conversion).

Keywords: ceria nanorods; copper-CeO₂; one-pot preparation; alcohol oxidation

1.-INTRODUCTION

Conventionally, stoichiometric oxidants are employed in the industrial process of alcohols oxidation. The oxidants are toxic and/or expensive, and large amounts of wastes are produced together with the desired product. Thus, the industrial processes associated to the oxidation of alcohols are among the most polluting and hazardous ones, with a high E-factor [1]. From an economic and an environmental point of view, the development of oxidation processes employing molecular oxygen and heterogeneous catalysts shows great advantages. Furthermore, the use of water as the solvent would fulfil all the requirements of a green oxidation process.

Noble metal catalysts, mainly gold and palladium ones, have been widely studied for alcohol oxidation in liquid phase. Au-based catalysts show excellent catalytic performance for the oxidation of alcohol in water, although the activity strongly depends on the presence of an added base [2]. Highly specific activities were reported for Pd on different materials for the benzyl alcohol oxidation in solvent free conditions [3,4]. However the selectivity to benzaldehyde is low when increasing conversion. Other high effective palladium based catalysts have been studied, employing organic solvents, [5], which increases E factor.

Catalysts based on earth-abundant, environmentally friendly and low-cost metals, as copper Cu, are highly attractive for industrial implementation. Generally first row metal based catalysts are less active than noble ones, and promoters or non inert supports should be employed in the formulations in order to develop suitable activity. Cerium dioxide (CeO_2) presents exceptional redox properties associated with the reversible $\text{Ce}^{3+}/\text{Ce}^{4+}$ redox couple, oxygen vacancies, acid and basic sites [6]. These features enable ceria to catalyze numerous reactions as alkylation and dehydration [7], ketonization [8, 9], hydrogenation [9], combustion [10] and Suzuki-Miyaura cross-coupling [11]. The properties of ceria give rise to peculiar metal-support interactions

when used in the formulation of heterogeneous catalysts, as for example for the liquid phase hydrodeoxygenation of vanillin [12]. Besides, a morphology effect of ceria on the catalytic behavior of Ag_2CrO_4 [13], Au [14], Pd [15], Ni [16], Pt [17], Ru [18] and Cu [19, 20] has been reported.

The production of benzaldehyde (bitter-almond flavour) is quite interesting since this aldehyde is widely employed in the cosmetics and flavour industries, and it is also a versatile intermediate in the synthesis of pharmaceuticals and agrochemicals [21]. Nowadays, there is no industrial process for producing benzaldehyde from a catalytic process, thus it would be of paramount importance to find a selective and active catalyst for carrying out the corresponding reaction, leading to a product which accomplishes the required quality of perfumery and pharmaceutical industry regulations [22].

Based on the above considerations, in the present study, copper catalysts supported on ceria were prepared, characterized and tested for the oxidation of benzyl alcohol in water. To our knowledge this kind of catalysts has not been studied for the production of benzaldehyde from benzyl alcohol.

Ceria samples were prepared by two methods, a direct combustion method and a hydrothermal synthesis leading to ceria nanorods. A series of copper-ceria materials were prepared following impregnation of these two different supports with $\text{Cu}(\text{AcAc})_2$. Besides, one-pot synthesis based on the direct combustion of copper and cerium salts was carried out for preparing other copper-ceria samples.

The characterization of the different catalytic materials was carried out with N_2 sorption, XRD, XPS, SEM, TEM, N_2O dissociative chemisorption and FT-IR. Finally an attempt to establish a relationship between the physicochemical properties of the materials and the corresponding catalytic pattern for the oxidation of benzyl alcohol in water was carried out.

2.-EXPERIMENTAL

2.1. Sample Preparation

The CC support was synthesized using a simple combustion method. A solution of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Aldrich, analytical reagent (AR) grade) and Sucrose (Aldrich, analytical reagent (AR) grade) was prepared. The cerium nitrate: sucrose: water weight ratio was 7.57:5.95:70. The solution was heated up to 400°C while stirring for producing combustion. The obtained solid was calcined at 400°C under chromatographic air during 2 h. In order to avoid contamination with carbonate, the sample was kept under a N_2 . This sample was named as CC.

Ceria nanorods (CNR) were synthesized by a hydrothermal method detailed in ref [23]. Briefly, a solution of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, in deionized water was precipitated with a NaOH solution (9.0 M). The mixture was stirred for 1 h at room temperature, and afterwards it was introduced in a Teflon vessel and placed inside a batch reactor for 24 h at 120°C . Following this procedure, the solid was washed with deionized water until neutrality, then dried in air flow at 70°C for 12 h and calcined under chromatographic air at 400°C for 3 h.

For preparing the copper-CC samples, two different methodologies were used: one-pot combustion and wet impregnation. $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Aldrich, analytical reagent (AR) Grade) were co-combusted following the same procedure than the one corresponding to CC synthesis. Two samples, with 5 and 20 wt% of nominal copper loading (Cu5CC and Cu20CC, respectively) were prepared using this procedure. Two other samples were obtained by wet impregnation of CC with a solution of $\text{Cu}(\text{AcAc})_2$ (Aldrich, analytical reagent (AR) grade) in toluene. These samples were named as Cui5CC and Cui20CC where the numbers 5 and 20 indicate the wt% nominal concentration of copper respectively.

The Cui5CNR and Cui20CNR copper catalysts were prepared by impregnating CNR with solutions of $\text{Cu}(\text{AcAc})_2$ in toluene, corresponding to target copper concentration of 5 and 20 wt% were employed.

2.2. Characterization

Copper concentration in the samples was measured by Atomic Absorption Spectroscopy (AAS) in a Perkin Elmer A-Analyst Equipment.

Samples were analyzed by X-ray diffraction (XRD) in a Bruker D-8 instrument, with $\text{CuK}\alpha$ radiation, within a 2θ range of $5\text{--}82^\circ$, with a scanning speed of $1.2^\circ/\text{min}$. For samples CC, Cu5CC, Cu20CC, the scanning speed was $0.019^\circ/\text{min}$ within of $5\text{--}82^\circ$ range, in order to perform a lattice parameter (a_0) estimation by means of Rietveld method. Textural characterization of the materials was carried out by N_2 adsorption at 77 K in Quantachrome Nova 1200e equipment. The specific surface areas (S_{BET}) were calculated employing the BET equation. Before measurements, a degassing of the solids for 4 h at 120°C was carried out. The morphology of the samples was examined by Scanning Electron Microscopy (SEM) on a Jeol JSM 35CF microscope. Transmission Electron Microscopy (TEM) images were taken in a JEOL 100X2 apparatus. Samples were also characterized by X-ray photoelectron spectroscopy (XPS) in a multi-technique Specs equipment provided with a Mg X-ray source. The samples were previously treated in the pre-chamber of the equipment under chromatographic Ar at 300°C . The analysis of Ce^{3+} and Ce^{4+} peaks was carried out in the 870–930 eV range of binding energies (BE). The charging correction was performed based on the C1s peak at 284.6 eV. $\text{Ce}^{3+}/\text{Ce}^{4+}$ atomic ratio were determined from the integrated deconvoluted peak area. Nitrous oxide dissociative chemisorption over copper catalysts was carried out for determining the copper metallic dispersion ($D\%$). Copper atoms at the surface were oxidized to Cu^{+1} with N_2O (5% $\text{N}_2\text{O}/\text{N}_2$) decomposition at 90°C for 20 min. The amount of oxygen associated to surface copper species, β , was measured by Temperature Programmed Reduction. Afterwards, bulk oxidation to Cu^{2+} was carried out at 300°C for 1 h under a 20% O_2/N_2 mixture, and the corresponding amount of oxygen, α , was

also measured by TCD detector [24]. The copper metallic dispersion, D%, was calculated with the following relationship: $D\% = \left(\frac{2\beta}{\alpha}\right) \times 100$ [24].

2.3. Oxidation of benzyl alcohol

The oxidation of benzyl alcohol was performed in a 50 ml Parr reactor. In a typical experiment, 0.250 g of catalyst was put in contact with a 0.1M aqueous solution of benzyl alcohol (30 ml of solution, 3 mmol of alcohol). The pressure was set at 0.34 MPa of chromatographic air, the stirring speed was 620 rpm and the reaction was considered to be started when the vessel reach 120°C. The experimental parameters of the reaction (temperature, air pressure, stirring rate, benzyl alcohol concentration) were selected following an optimization procedure in order to get effective results. Aliquots of the reactive mixture were removed periodically by a sampling system and a quantification of reactant and products was carried out by gas chromatography with a FID detector, using a capillary column (ZB-5. 30m length, 0.25 ID and 0.25 μm film thickness). Additionally, samples were analyzed in a Perkin-Elmer Claurus 500 chromatograph, provided with a mass spectrometry detector. The conversion of benzyl alcohol and the selectivity to benzaldehyde were calculated along with time. The integrated activity of the catalysts, expressed as mole of benzyl alcohol converted per gram of copper following 6 h of reaction time, was also calculated.

Sheldon test was carried out to determine if homogenous species of copper and or ceria were present in the reaction media. At 1 h of reaction time the catalysts was separated by hot filtration from the reaction media, and the absence of activity in the free catalysts condition was checked. The reuse of the catalysts was studied. Following a reaction test, the spent catalyst was recovered by filtering and it was washed with distilled water. The solid was dried at room temperature and tested again.

3.-RESULTS

3.1 Catalyst characterization

Figs. 1 a-d show SEM and TEM images corresponding to CC and CNR ceria samples. It is observed that ceria obtained by the combustion method shows an irregular surface plenty of non-uniform cavities with sizes in the 0.2 to 5 μm range, while CNR is constituted by rods with diameter between 20 and 50 nm. In the CC sample, the cavities could be formed during the release of NO_x and CO_2 produced by the combustion and decomposition of the precursor salts. The specific surface areas of CC and CNR, calculated from BET method (S_{BET}) were 36 and 61 m^2/g , respectively.

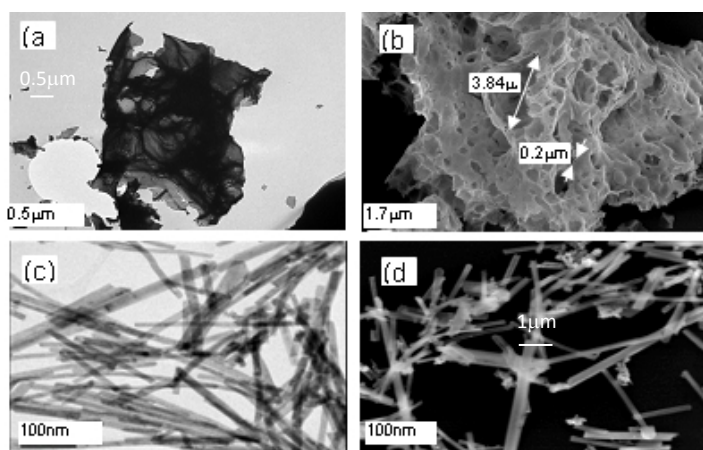


Figure 1. Micrographs of ceria. (a) TEM image of CC, (b) SEM image of CC, (c) TEM image of CNR, (d) SEM image of CNR

For both CC and CNR, typical XRD diffraction patterns corresponding to a face centered cubic fluorite structure of ceria ($\text{Fm}\bar{3}\text{m}$; JCPDS card N° 34-0394) were observed in Figs. 2a and b. No other diffraction peaks than those corresponding to cerium oxide were detected in these patterns.

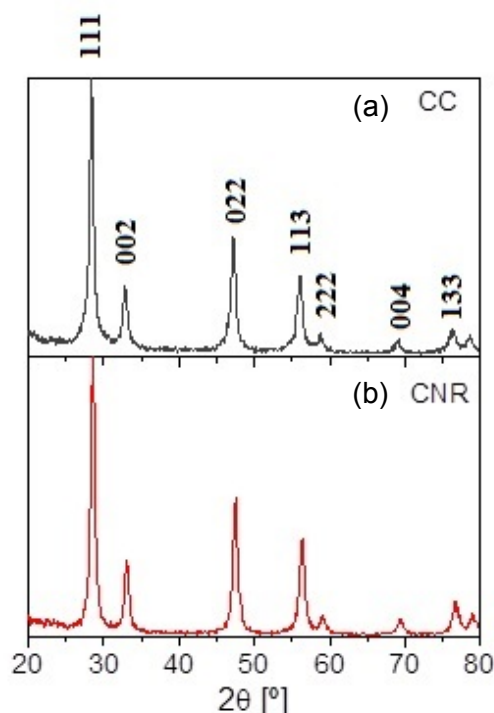


Figure 2. XRD pattern of ceria supports: (a) ceria prepared by combustion, CC and (b) ceria prepared by hydrothermal synthesis, CNR.

Fig. 3 displays the XRD spectra of copper-ceria materials. In the patterns of the Cu20CC, Cu5CC and Cu10CC samples the characteristic peaks of a secondary phase corresponding to CuO (tenorite) are observed.

Lattice parameters of CC, Cu20CC and Cu5CC were estimated by means of Rietveld method. The lowest agreement of fitting in this procedure was $\chi^2=1.9$, indicating a quite accurate representation of the diffraction profiles. From this fitting procedure, the amounts of tenorite phase were 4.3 and 13.8 wt%, for Cu5CC and Cu20CC respectively. It is reasonable to assume that, the difference between the metal loadings measured by AAS (4.8 wt% of copper for Cu5CC and 18.1wt% of copper for Cu20CC) and the values estimated from Rietveld approximation would correspond to highly dispersed copper species which do not originate diffraction peaks. Thus two copper

species are present in both the Cu20CC and Cu5CC catalysts: CuO bulky particles and highly dispersed copper species.

Besides, from Rietveld estimation it was calculated that the lattice parameter, a_0 , increases with the copper loading (see Table 1). This result suggests that highly dispersed copper species are located at interstitial sites instead of substituting cerium cations, as was previously reported [25,26]. This result affects the crystallite size, 9.55 nm and 10.04 nm for Cu5CC and Cu20CC respectively.

On the other hand, for the Cu5CC and Cu5CNR samples, the XRD profiles were quite similar to the ones corresponding to the ceria materials (CC and CNR) and the peaks due to CuO particles were not detected. The absence of diffraction peaks corresponding to copper species would be related with the high dispersion that this metal can achieve over ceria surface in these samples. In line with this, Du et al. observed high dispersions of copper up to 30% of metal loading [27], while Mallesahm et al. concluded that cerium species notably inhibit the crystal growths of CuO [20]

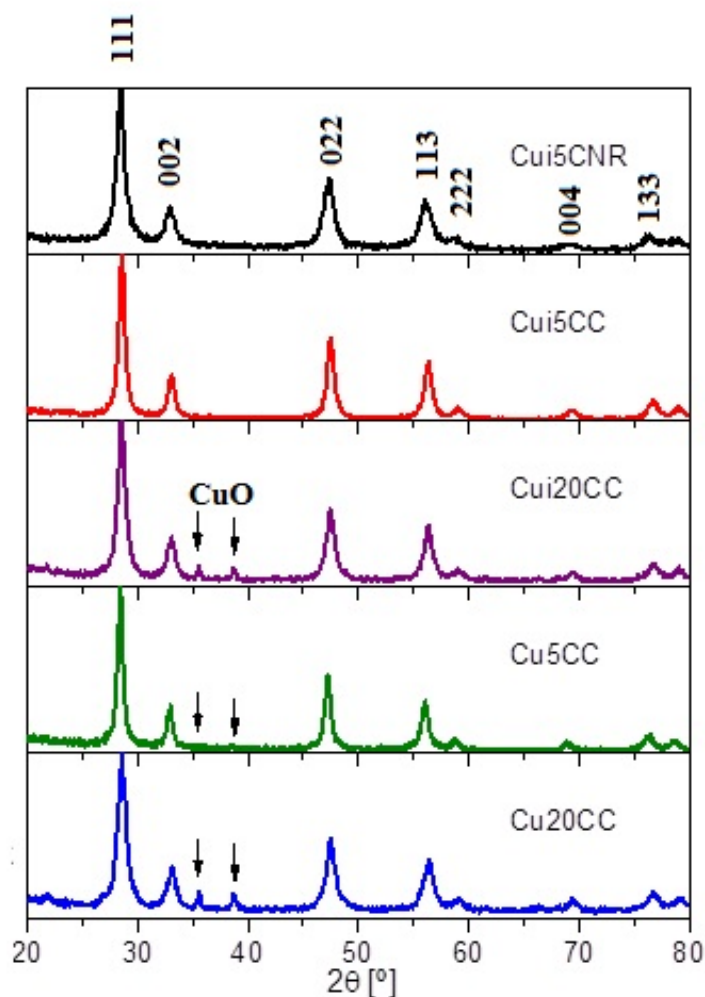


Figure3 . XRD pattern of Cui5CNR, Cui5CC, Cui20CC, Cu5CC and Cu20CC samples.

Regarding the N_2 sorptometry characterization of the samples, a slight increase in the BET specific surface area of the Cu5CC sample was observed by comparison with the bare support. On the other hand, the samples prepared by impregnation of CC and CNR, (Cui5CC and Cui5CNR) do not significantly change the surface area of the original ceria. On the contrary, for high copper loading (i.e, Cui20CC and Cui20CNR), the area is depleted from 36 to 23 m^2/g and from 61 to 18 m^2/g , respectively. The noticeable decrease of the surface area of CC would be related with the blockage of the porous structure of this material.

The copper dispersion (D%) was measured by dissociative N_2O chemisorption for some of the samples (see Table 1). The lowest values (0.5%) are achieved for both Cui20

samples. In these cases, the high copper loading gives rise to the formation of large CuO crystals and concomitantly, to extremely low copper dispersion. On the contrary, a 5% copper loading, as in the case of both Cui5 samples, originates high copper dispersions on the ceria surface, giving rise to values of 75-78%. For Cu5CC, a low copper dispersion was observed (16%), which is linked to the preparation method of this sample: The co-combustion of copper and cerium nitrates originates metal species being buried in ceria. The same conclusion is valid for Cu20CC, which also presents copper species buried inside ceria.

Table 1. Physicochemical properties of the Cu-CeO₂ samples

Sample	Cu wt% ^a	S _{BET} (m ² /g)	Cu D% ^b	Ce ³⁺ /Ce ⁴⁺ ^c	a ₀ (nm) ^d
CC	-	36	nd ^e	0.11	0.54123
CNR	-	61	nd	Nd	0.54215 ^f
Cu5CC	4.8 (0.5) ^g	44	16	0.16	0.54126
Cu20CC	18.1 (4.7) ^g	35	38	0.17	0.54130
Cui5CC	4.7	36	78	0.15	nd ^e
Cui20CC	17.2	23	0.5	0.10	nd
Cui5CNR	5.5	62	75	Nd	0.54143 ^f
Cui20CNR	18.5	18	0.5	Nd	nd

^aCopper content by AAS, ^bCopper dispersion (%) measured by N₂O chemisorption, ^cCe³⁺/Ce⁴⁺ atomic ratio calculated from integrated area from XPS peaks, ^d Lattice constant from Rietveld analysis, ^e not determined, ^ffrom reference [23], ^gcopper wt% in ceria lattice estimated from Rietveld calculation,

The chemical nature of the copper-ceria interaction was further studied by XPS, focusing the attention on the cerium 3d peaks. Fig. 4 shows the XP transitions appearing in the 875–927 eV range for CC, Cu20CC, Cu5CC, Cui5CC, Cui20CC and for CuO / CC mechanical mixture. The peaks named as v₀, v₁, v₂, v'₀, and v'₁ were assigned to Ce⁴⁺, while the other peaks (u₀, u₁, u'₀, and u'₁) were attributed to Ce³⁺ [28]. The relative amount of Ce³⁺ and Ce⁴⁺ species, expressed as Ce³⁺/Ce⁴⁺ atomic ratio, was estimated for CC and CNR and for six selected samples. The atomic ratio was obtained from the area of the peaks corresponding to Ce³⁺ and to Ce⁴⁺ detailed above. It is worth to note that

$\text{Ce}^{3+}/\text{Ce}^{4+}$ atomic ratio (see fourth column of Table 1) is higher for the Cu-CeO₂ samples than for the CeO₂ ones and also than for the mechanical mixture. At this point it is interesting to note that Sudarsanam et al. have concluded, based on XPS and Raman studies, that the decoration of copper oxide on CeO₂ nanocubes leads a higher concentrations of Ce^{3+} ions [29]

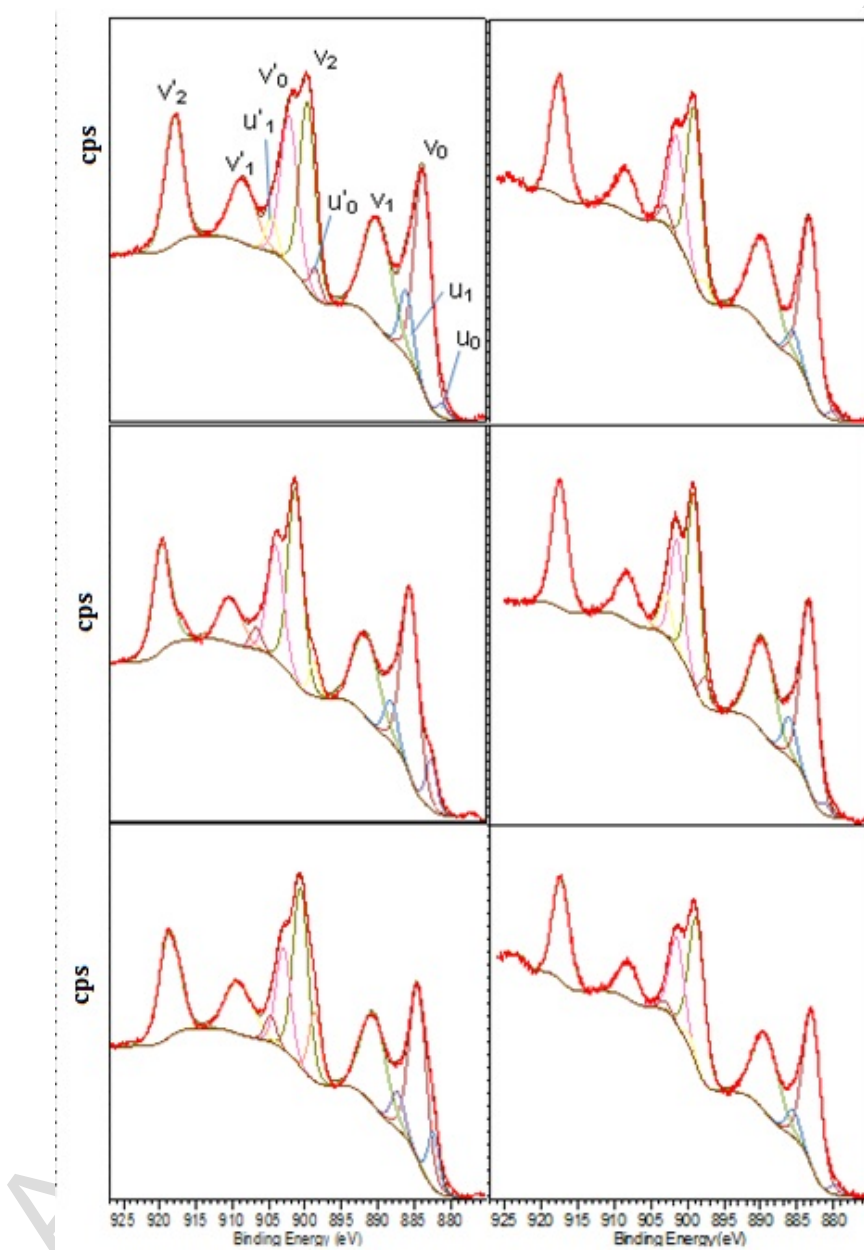


Figure 4: X-ray photoelectron spectra, of Ce 3d.(a):CC;(b):Cu5CC; (c): Cu20CC; (d):CuO-CC mechanical mixture;(e):Cui5CCand; (f): Cui20CC.

Samples with large copper crystal sizes, as Cui20CC, develop low copper dispersion and similar Ce^{3+}/Ce^{4+} ratio than the pure ceria, or than the CuO-CC mechanical mixture. On the other hand, the Cui5CC, Cu5CC, and Cu20CC samples, with high copper dispersion over ceria, develop relatively high Ce^{3+}/Ce^{4+} ratio.

3.2 Catalytic test: oxidation of benzyl alcohol in water

A previous blank test indicated that no reaction takes place in the absence of the catalysts. The Cu20CC sample was employed to check that the reaction was not diffusion limited under the experimental conditions. The conversion of benzyl alcohol following 1 h of reaction time, increases linearly with the weight of the catalyst in the 0.1-0.4 g range, showing that external diffusion limitations are absent for the reaction conditions employed in the reaction test of the present study.

The catalytic properties of the solids are reported in Table 2. Both ceria samples, CC and CNR, developed low conversion levels (2-4%) following 6 h of reaction (see Table 2, second column).

The Cui20CC and Cui20CNR samples also presented low activity, reaching conversion levels similar to the supports. On the other hand the rest of copper catalysts were more active than the corresponding pure ceria.

Table 2. Catalytic properties of Cu-CeO₂ materials ^a.

Catalyst	Conversion ^b (%)	Selectivity ^c (%)	Activity ^e (mol/gCu)
CC	2	100 ^d	-
CNR	4	100 ^d	-
Cu5CC	18	100 ^d	0.04
Cu20CC	60	90	0.04
Cui5CC	41	85	0.10
Cui5CNR	48	73	0.10

^areaction conditions: 0.250 g of catalyst, T = 120 °C, pO₂ = 10 bar, stirring rate 650 rpm, distilled water as the solvent, ^bconversion (%) of benzyl alcohol at 6 h of reaction time, ^cselectivity (%) to aldehyde at 40% of conversion, except for ^dwhich corresponds to a lower conversion value, ^e integrated activity expressed as mole of benzyl alcohol converted per g of copper following 6 h of reaction time.

The dependence of conversion and selectivity on time for Cu5CC, Cu20CC, Cui5CC and Cui5CNR is shown in Fig. 5.

High conversion is reached by Cu20CC, while the other two catalysts with similar copper content, Cui20CC and Cui20CNR, were practically inactive (results not shown in Fig. 5). This is explained by the presence of large copper oxide crystals and to the low metal-ceria interaction in Cui20CC and Cui20CNR, as concluded from the results of N₂O dissociative chemisorption ($D\% < 0.5\%$) and XPS (Ce^{3+}/Ce^{4+} ratio similar to the one corresponding to the bare support). Cu5CC developed lower activity than their counterparts with similar copper loading, Cui5CC and Cui5CNR. The relative low activity of Cu5CC would be related with the one-pot synthesis utilized for preparing this sample which originates a fraction of inaccessible copper to reaction embedded in ceria support. Turning the attention to the Cui5CC and Cui5CNR catalysts, the catalytic activity of both samples is quite similar. This could be related to the high concentration of highly dispersed copper available at the ceria surface (see $D\%$ values in Table 1).

The values of the integrated activity, calculated as mole of benzyl alcohol converted per g of copper during 6 h of reaction time, are reported in Table 2, last column. It is worth to note that both samples prepared by the combustion method (Cu5CC and Cu20CC) show the same value of integrated activity (0.04 mole/g Cu). On the other hand, the Cui5CC and Cui5CNR samples both present a higher value, 0.1 mole/g Cu. The highest specific activity for impregnated samples is due to the fact that the whole of the copper loading is located at the ceria surface while for the samples prepared from the one-pot combustion method, a fraction of copper remains in the bulk of the catalysts.

The activity values achieved by Cui5CC, Cui5CNR, Cu5CC and Cu20CC are relatively high considering that copper is a rather inactive metal for oxidation of alcohols. To assess the promotional effect of the support on the activity, a copper catalyst on SiO₂ was tested under the present reaction conditions. Silica support practically shows no redox active sites, neither noticeable acidic nor basic sites. With this in mind, a Cu/SiO₂ sample with copper loading of 8wt%, previously studied by some of us [30], was evaluated for the oxidation of benzyl alcohol in water. The conversion level reached by this sample was practically null (1%), showing that the intrinsic activity of copper for carrying out the oxidation of benzyl alcohol in water is extremely low. In conclusion, a promotional role of both ceria supports, CC and CNR on the catalytic properties of copper is present in copper ceria catalysts. It could be argued that redox properties of ceria, associated with the Ce^{3+}/Ce^{4+} couple, play a crucial role in the enhancement of the copper activity, by the activation of the alcohol molecule in the first step of the reaction.

Turning the attention to the selectivities, the results are reported in Table 3 and in Figs. 5. All the catalysts showed 100% of selectivity at low conversion values. As conversion increased, the selectivity values diminished for all the samples, but for Cui5CC. Other detected products than benzaldehyde were benzoic acid, toluene and benzyl benzoate. Distribution of these products at approximately 40% level of conversion is reported in Table 3 for Cu20CC, Cui5CC and Cui5CNR.

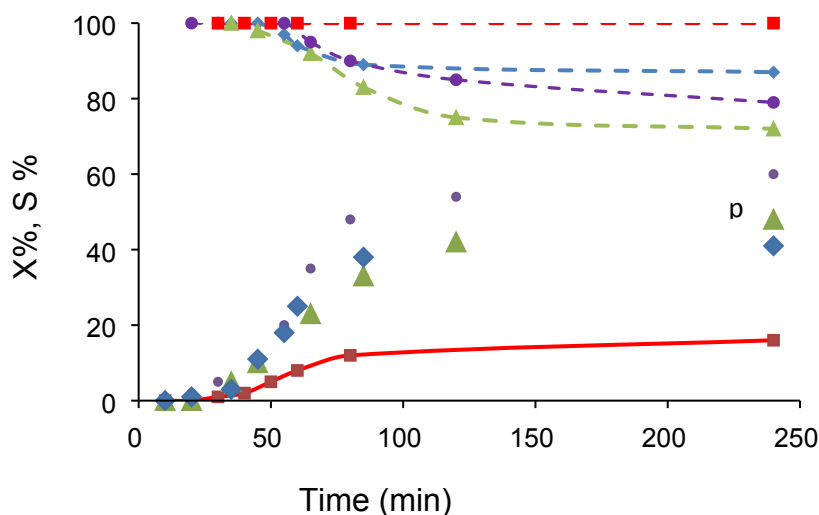


Figure 5. Dependence of percentage of conversion (X%) ___ of Cu20CC (●), Cui5CNR (▲), Cui5CC (◆), Cu5CC (■) and selectivity (S%) to benzaldehyde of Cu20CC (●), Cui5CNR (▲), Cui5CC (◆), Cu5CC (■) on time. Reaction conditions: 0.250 g of catalyst, $T = 100\text{ }^{\circ}\text{C}$, $p\text{O}_2 = 10\text{ bar}$, stirring rate 650 rpm, distilled water as the solvent

Table 3. Selectivities (%) in the benzyl alcohol oxidation at approximately 40% of conversion^a.

Catalyst	$S_{\text{benzaldehyde}}$	$S_{\text{benzoic acid}}$	S_{toluene}	$S_{\text{benzyl benzoate}}$
Cu20CC	90	9	1	0
Cui5CC	85	10	2	3
Cui5CNR	73	10	5	11

^aReaction conditions: 0.250 g of catalyst, $T = 100\text{ }^{\circ}\text{C}$, $p\text{O}_2 = 10\text{ bar}$, stirring rate 650 rpm, distilled water as the solvent

When selectivities are compared at the same level of conversion of 40%, Cu20CC shows the highest selectivity towards benzaldehyde. The selectivity to the desired product in this case is 90%, while over oxidation is also detected, with a selectivity of 10% to benzoic acid. Cui5CNR presents the lowest selectivity, mainly due to the fact

that besides the production of benzoic acid, this sample also promotes a condensation reaction, leading to benzyl benzoate. Furthermore, another product is also present: toluene (a cracking product), with a selectivity of 5%.

Benzoic acid production is almost the same for the three samples, Cui5CNR, Cui5CC and Cu20CC, thus almost the same concentration of active sites for over oxidize the aldehyde would be present for these samples. On the other hand, condensation and cracking reactions occur in the highest extend for the case of the Cui5CNR sample. It is well known that condensation and cracking reactions are catalyzed over acid sites, thus it could be postulated that the surface of Cui5CNR sample shows higher acidic properties than both Cui5CC and Cu20CC. Furthermore, the formation of byproducts was not detected for Cu20CC, even for high conversion levels (60%).

For further investigate on the acidic nature of the catalytic surface of Cu20CC and Cu5iCNR, a TPD of NH_3 analysis was carried out (Fig.6). The TPD profile of CNR presents a signal which corresponds to $1171\mu\text{mol g}^{-1}$ of NH_3 evolved, indicating that the surface of the sample shows acidic sites. On the other hand, for the profile of C a minor amount of the base evolved ($154\mu\text{mol g}^{-1}$).

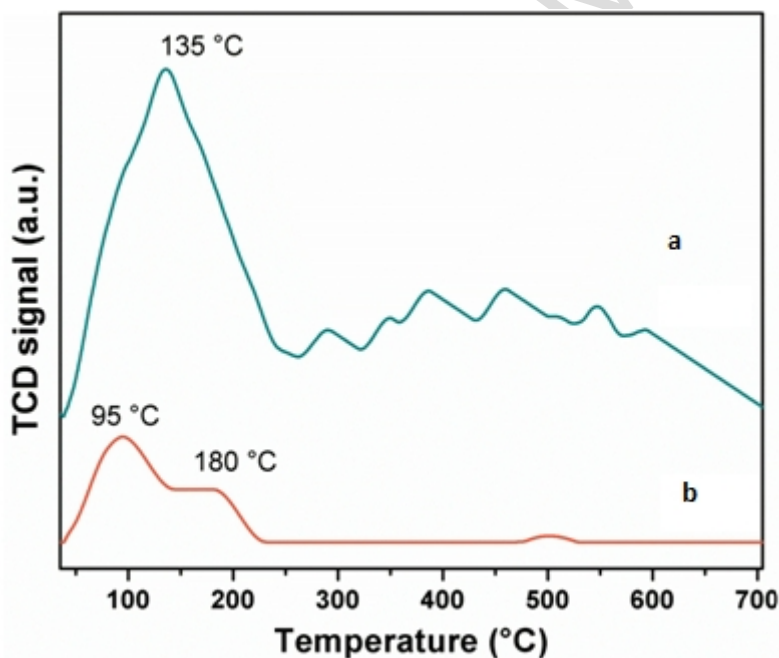


Figure 6. TPD of NH_3 for (a) Cui5CNR, and (b) Cu20CC

Summing up, Cu₂₀CC should be considered as the material with the best performance for the oxidation of benzyl alcohol to benzaldehyde in water among the catalyst prepared in the present study. Its activity is quite high (0.04mole of alcohol converted per g of Cu) and the selectivity to the desired products reaches 90%. Its low surface acidity hampers undesired reaction of cracking and condensation. It could be postulated that the mechanism for the oxidation of benzyl alcohol over Cu₂₀CC starts with the activation of the alcohol on supports sites, followed by a oxidation to benzaldehyde over copper/ceria interhphase. Due to the strong oxidation properties of this site a low production of benzoic acid could not be avoided. For the case of supports with high acid sites concentration (as in the case of CNR samples), cracking and condensation reaction also takes place, diminishing the selectivity to benzaldehyde

To our knowledge, one of the highest activity in oxidation of benzyl alcohol was obtained with Pd/hydroxyapatite, at 90°C and atmospheric O₂ pressure (TOF value of 500h⁻¹) [31]. In this sense, Cu₂₀CC is less active, but it is worthy to note that this catalyst works in water, not in an organic solvent as in the case of Pd/hydroxyapatite.

4.CONCLUSIONS

A series of Cu-CeO₂ materials prepared by hydrothermal synthesis and by a one-pot combustion from cerium and copper nitrates were prepared, characterized and tested for the oxidation of benzyl alcohol in water. The prepared samples show varied copper dispersion, redox and acidic properties, depending on their composition and on the preparation method.

All these properties strongly influence on the catalytic behavior of the Cu-CeO₂ samples evaluated for the oxidation of benzyl alcohol in water. The catalysts with high surface Cu-Ce³⁺ concentration were quite active, while surface acid sites would lead to undesired reaction which decreases selectivity to benzaldehyde. The best performance for the oxidation of benzaldehyde to benzyl alcohol is attained for samples with high Cu-Ce³⁺ and low surface acidity. These conditions were attained by the sample prepared by a simple one-pot combustion synthesis, with 18wt% of copper, which shows high activity and selectivity(90%, at 40% of conversion).

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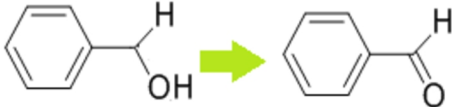
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Declarations of interest: none

ACCEPTED MANUSCRIPT

- Catalysis based on non noble metals for production of benzaldehyde are studied
- Copper/ceria are prepared, characterized and tested for alcohol oxidation.
- Copper (20wt%) /ceria prepared by co-combustion leads to a selective catalysis in water

ACCEPTED MANUSCRIPT



-   Ce^{3+}
-  CuO
-  Acid Sites
-  Bulk CuO (B)

