

2-Chlorophenol degradation by catalytic wet air oxidation using copper supported on $\text{TiO}_2\text{-CeO}_2\text{-ZrO}_2$

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ABSTRACT

In this work, we describe the morphological, electronic and catalytic properties of support $\text{TiO}_2\text{-CeO}_2\text{-ZrO}_2$, prepared by sol-gel method, which was impregnated with copper at 5 and 10% by weight, in order to obtain efficient catalysts in the catalytic wet air oxidation (CWAO) of 2-cp. The catalysts were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM-EDS), UV-Vis diffuse reflectance spectroscopy (DRS) and nitrogen physisorption by the Brunauer-Emmett-Teller (BET) method. The activity of the materials used in this study revealed that without the presence of Cu, the SCO_2 is low and with a content of 10% this metal shows the best catalytic behaviour; conversely, a reaction mechanism is proposed that describes the complete oxidation of 2-cp in this case.

Key words | 2-Chlorophenol, copper, CWAO, Nanoparticles, $\text{TiO}_2\text{-CeO}_2\text{-ZrO}_2$

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INTRODUCTION

At present, environmental pollution is of international relevance. It is generated mostly by the large industries, among these the most prominent are the textile and the pesticide sectors, since their residues are poured out into the aquatic layers without having effective treatment and causing severe damage to living beings (Li *et al.* 2011).

2-Chlorophenol (2-Cp) is an organic compound that is found within the waste of textile and pesticide industries; these compounds are widely used as wood preservative agents, paintings and plant fibres, disinfectants and intermediates, and they are known as a group of higher toxic pollutants (Alfano *et al.* 2001; Pi *et al.* 2007; Li *et al.* 2011).

Several remediation techniques have been proposed to solve the problem of the effects generated in the water environment; various organic compounds originating from

industries have been treated by some of these processes, such as conventional biodegradation, since it is an economical process, but it is sensitive to shock charges and requires a long hydraulic retention time (Li *et al.* 2011).

Advanced oxidation processes are other methods used where catalytic wet air oxidation (CWAO) is more effective than classic oxidation. CWAO is based on oxidation with molecular oxygen in the liquid phase at lower temperatures and pressures, the pressures used range between 10 and 200 bars, and the temperature is between 150 °C and 350 °C (Stüber *et al.* 2005; Yang *et al.* 2008). To solve this problem, some highly active catalysts should be found. In recent years, various catalysts have been developed for CWAO of chlorophenols. Chang *et al.* (1995) compared the activities of CuSO_4 , MnO_2 and Co_2O_3 in the CWAO of 4-CP at the

temperature range of 49.85 °C–199.85 °C. The research found that CuSO₄ is the most effective catalyst and that alkaline conditions favour 4-CP degradation.

This paper presents a study of Cu materials synthesis, supported in mixed oxide (TiO₂-CeO₂-ZrO₂) in addition to the catalytic evaluation of the 2-Cp, through CWAox, by increasing the % of Cu on the materials.

EXPERIMENTAL

Materials synthesis

Preparation of the mixed oxide TiO₂-CeO₂-ZrO₂ by sol-gel method

TiO₂-CeO₂-ZrO₂ supports with concentrations of 50 wt% TiO₂, 5 wt% CeO₂ and 45% ZrO₂ by weight, were synthesized by the sol-gel method. The sol-gel process is based on simultaneous chemical reactions of hydrolysis and condensation. Alkoxide hydrolysis can be catalyzed by an acid or a base where the sols are obtained. The gel is formed in the drying time called ageing (Ramírez Palma *et al.* 2010). It was synthesized in a hydrolysis between titanium butoxide (Sigma-Aldrich (Ti(OC₄H₉)₄) 80 wt% in 1-butanol) and zirconium butoxide, (Sigma-Aldrich (Zr(OC₄H₉)₄) 80 wt% in 1-butanol) with ultra-pure water and 1-butanol (Sigma-Aldrich, CH₃(CH₂)₃OH) 98%) as solvent medium) using the molar relationships between the reagents:

Alkoxide/Water = 1/16 and Water/Alcohol = 1/8

Cerium nitrate (III) hexahydrate (Ce(NO₃)₃·6H₂O) Sigma-Aldrich (99%)) was mixed with water that represented three times the volume of the precursor, 5 drops of ammonium hydroxide (NH₄OH) (from Sigma-Aldrich, 28% into water) were added as a hydrolysis catalyst. It was dried at a temperature of 120 °C, then calcined with a heating ramp from 2 °C/min to 500 °C for 24 h.

Preparation of Cu-containing materials

The synthesis of the Cu-containing materials was done by the impregnation method, which uses a metallic solution that is deposited on the surface of a support, in this case, the precursor of Cu was the hydrated copper (II) nitrate Cu(NO₃)₂·2.5H₂O (from Sigma-Aldrich, 98%), mixed with ultrapure water (at triple volume depending on the amount

of the support employed), with constant stirring and at room temperature.

Subsequently, it was introduced to a rotavapor as a drying process in order to extract the produced liquid. It was completely dried in an oven at a temperature of 120 °C for 24 hours to remove all the organic residues the sample might have had. For its oxidation, it was calcinated at a heating ramp of 2 °C per min up to 400 °C (Dong *et al.* 2013). The necessary quantities of the Cu precursor were calculated to obtain materials containing Cu at 5 and 10 wt% respectively.

Characterization techniques

N₂ physisorption

The determination of specific area, pore diameter and volume of the catalysts was carried out by the N₂ physisorption technique using the Brunauer-Emmett-Teller (BET) method. Measurements were performed using MICROMERITICS TRISTAR 3020 II at 77 K (–196 °C). In a typical measurement, 0.2 g was weighed and degassed in N₂ ambient during 2 hours at 300 °C to remove impurities.

X-ray diffraction (XRD)

XRD analysis was realized using a Bruker Advance D8 X-ray diffractometer at the following conditions: a radiation source of CuKα, at λ = 1.790307 Å; 30 kV and 15 mA.

Scanning electronic microscope (SEM)

The images were obtained in the SEM equipment, VP Philips XL 30 model, equipped with an energy dispersive spectroscopy (EDS), backscattered electrons and secondary electron detectors for imaging. The scenario is not motorized. SEM is operated through a PC-based system.

UV-Vis spectroscopy

The diffuse reflectance spectra, UV-Vis, were obtained in the range of 190–900 nm with diffuse reflectance accessory (sphere coupled integration). The BaSO₄ compound was used as a reference with 100% reflectivity in a 300 Varian Cary spectrophotometer operating at room temperature.

Catalytic activity

The 2-Cp wet oxidation experiments were performed in a 600 mL stainless steel Parr reactor. The tests were performed at 160 °C and partial pressure of 15 bar, using oxygen as an oxidizing agent, in addition to a vigorous stirring at 1,000 rpm to avoid external diffusion problems during the reaction period. A solution of 150 mL was added to a 2-Cp concentration of 1,000 ppm using a catalyst ratio of 1 g/L of an aqueous solution. Samples were taken at different times. The 2-Cp degradation was determined by high-resolution liquid chromatography.

A Chromatograph Shimadzu Prominence HPLC was utilized for the above mentioned. Total Organic Carbon (TOC) was used; it is a global parameter with the ability to assess the elimination of pollutants in water. A Shimadzu TOC-VCHS analyzer equipment, TOC-LCSN model, was employed to determine the TOC.

RESULTS

Characterization

N₂ physisorption (BET surface areas)

Figure 1 shows that all the materials are type IV, this is characteristic of the mesoporous solids, with a type H2 hysteresis loop according to the IUPAC classification that determines the pore geometry, associated with inkwell form pores (a wide cavity surrounded by narrows or necks) and in which the effect of blocking pores is presented. This arises the percolation (cavitation) of the vapour phase, represented by the abrupt fall of the adsorption branch. (Hernández-Pichardo & Cedeño Caero 2014).

At the beginning of this type of isotherm, it is attributed to the initial part of the adsorption in the monolayer-multilayer.

Figure 2 shows the pore size distribution of the supports and the catalysts; a bimodal behaviour can be observed, corroborated with the peaks obtained in the result. The average diameter of pore was 5.6 nm for the support (TiO₂-CeO₂-ZrO₂) and an average pore volume of 0.57 cm³/g, this varies depending on the metallic charge of copper, see Table 1.

Scanning electron microscope (SEM)

Figure 3 shows the scanning electron microscope images and the EDS of the catalysts TiO₂-CeO₂-ZrO₂, Cu(5%)/TiO₂-CeO₂-ZrO₂ and Cu(10%)/TiO₂-CeO₂-ZrO₂. A completely

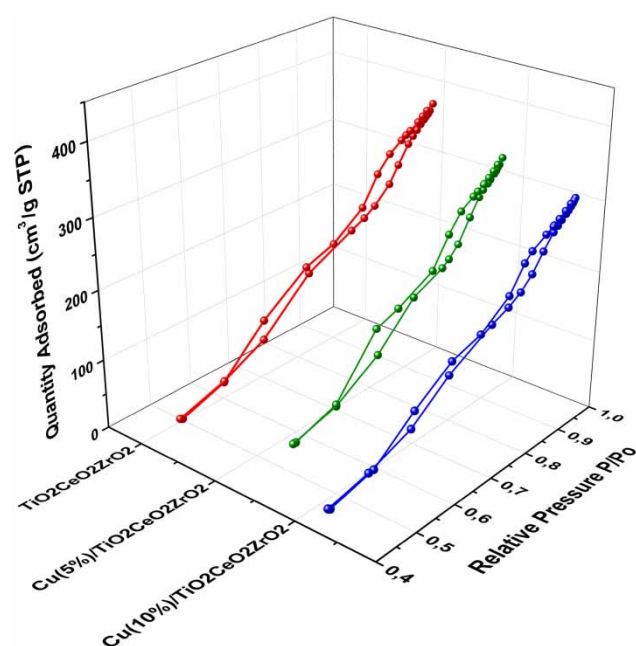


Figure 1 | N₂ adsorption-desorption isotherms of materials.

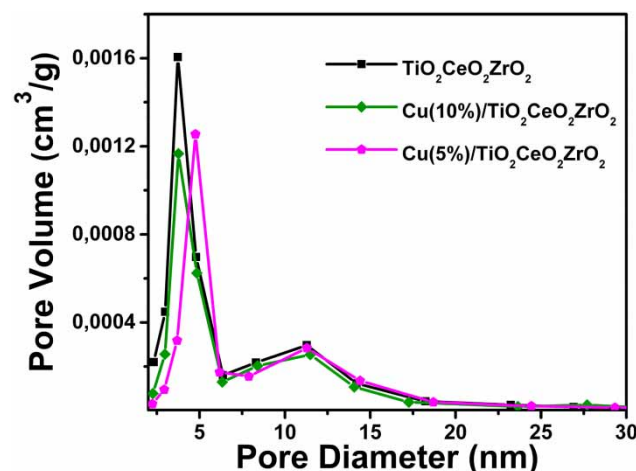


Figure 2 | Pore size distribution of materials by BJH method.

Table 1 | Specific surface area, pore average diameter and pore average volume of the support and monometallic catalysts by BET method

Catalyst	Specific surface area (BET)	Pore average diameter	Pore volume average
TiO ₂ -CeO ₂ -ZrO ₂	291 m ² /g	5.6 nm	0.57 cm ³ /g
5 Cu ⁰ %/TiO ₂ -CeO ₂ -ZrO ₂	203 m ² /g	6.6 nm	0.47 cm ³ /g
10 Cu ⁰ %/TiO ₂ -CeO ₂ -ZrO ₂	220 m ² /g	6.0 nm	1.45 m ³ /g

heterogeneous morphology of the material can be observed, confirming what was expected for the materials, there are

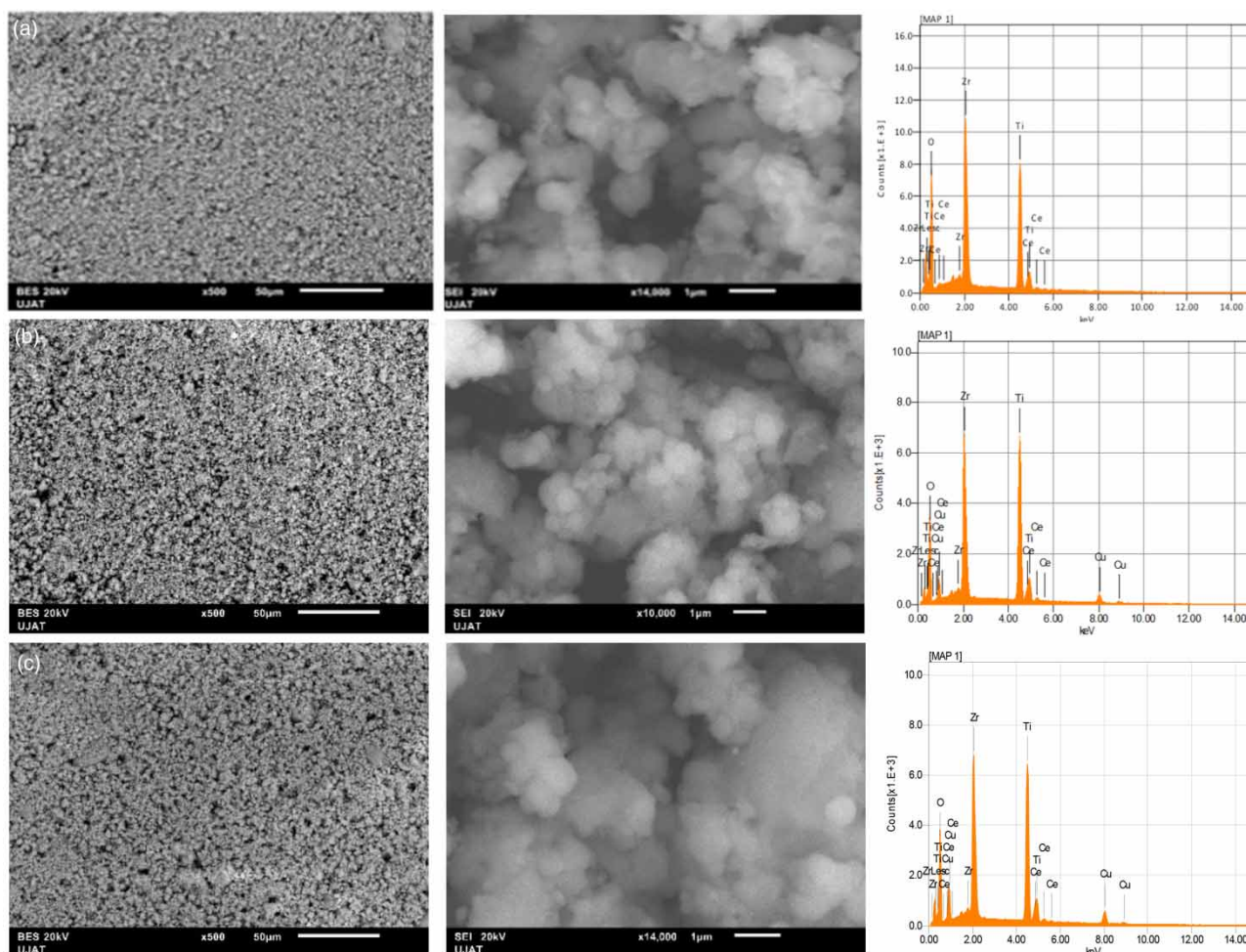


Figure 3 | SEM micrographs and EDS analysis of (a) $\text{TiO}_2\text{-CeO}_2\text{-ZrO}_2$, (b) Cu at 5 wt% supported on $\text{TiO}_2\text{-CeO}_2\text{-ZrO}_2$ and (c) Cu with 10 wt% supported on $\text{TiO}_2\text{-CeO}_2\text{-ZrO}_2$.

no relevant differences between the support and the catalysts since they practically have the same morphology.

Regarding the quantification by EDS, in the analyzed areas of the support $\text{TiO}_2\text{-CeO}_2\text{-ZrO}_2$ (see Table 2), it was found that the actual content is slightly lower than the theoretically calculated amount, decreasing the percentages by weight of Ti, Ce and Zr. It is possible to observe that the actual amount of metal is also less than the theoretical calculated amount with the addition of the metal Cu at 5% and Cu at 10% by weight of metal, by impregnation method, being 3.59% in Cu (5%) and 7.19% in Cu (10%) respectively (see Table 2).

Table 2 | Elementary chemical composition obtained by energy-dispersive X-ray spectroscopy (EDS) of the materials $\text{TiO}_2\text{-CeO}_2\text{-ZrO}_2$, Cu(5 wt%)/ $\text{TiO}_2\text{-CeO}_2\text{-ZrO}_2$, Cu(10 wt%)/ $\text{TiO}_2\text{-CeO}_2\text{-ZrO}_2$

$\text{TiO}_2\text{-CeO}_2\text{-ZrO}_2$		Cu(5 wt%)/ $\text{TiO}_2\text{-CeO}_2\text{-ZrO}_2$		Cu(10 wt%)/ $\text{TiO}_2\text{-CeO}_2\text{-ZrO}_2$	
Element	wt%	Element	wt%	Element	wt%
O	45.25	O	41.24	O	34.17
Ti	22.19	Ti	25.51	Ti	26.80
Zr	29.83	Zr	28.59	Zr	28.09
Ce	2.73	Ce	3.06	Ce	3.74
Total	100	Cu	3.59	Cu	7.19
		Total	100	Total	100

UV-Vis (DRS) spectroscopy

Figure 4 shows the UV-Vis DRS spectrum of the catalysts $\text{TiO}_2\text{-CeO}_2\text{-ZrO}_2$, Cu(5%)/ $\text{TiO}_2\text{-CeO}_2\text{-ZrO}_2$ and Cu(10%)/ $\text{TiO}_2\text{-CeO}_2\text{-ZrO}_2$. TiO_2 has a wavelength of

407 nm, 3.05 eV, (Hernández Enríquez *et al.* 2008), there is oxide in this region, the results show a displacement of the signal a little behind the wavelength 375 nm resulting from the presence of various oxides. ZrO_2 has a 230 nm

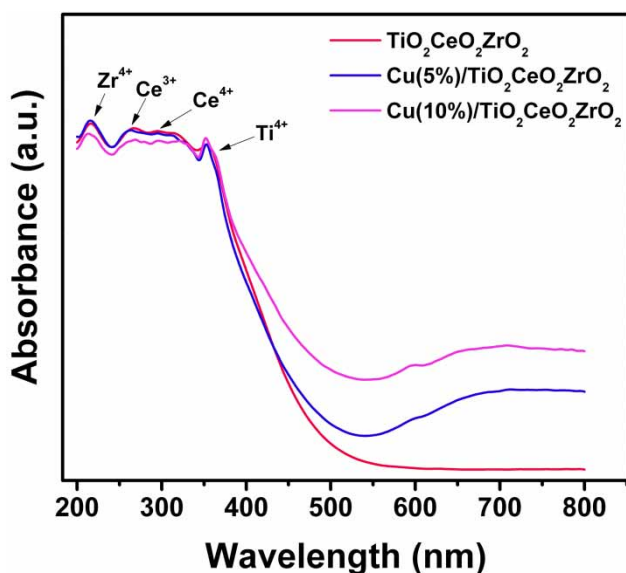


Figure 4 | UV-Vis DRS spectrum of materials.

wavelength; its presence is very clear because of the well-defined peak, showing the tetragonal and monoclinic phases (Molina-Pérez *et al.* 2006).

Ce is presented in a wide range; besides a coexistence of Ce^{4+} and Ce^{3+} , there are two types of characteristic bands at 250 and 297 nm and the reflected spectrum can be clearly seen, additionally, it is an n-type semiconductor with a 3.1 eV band of banned energy (Bandgap). Cu presents a wavelength of 605 nm, the signal is not very intense, but it is characteristic of this metal (He *et al.* 2010).

X-ray diffraction (XRD)

Figure 5 shows the XRD patterns of the catalysts $\text{TiO}_2\text{-CeO}_2\text{-ZrO}_2$, $\text{Cu(5\%)/TiO}_2\text{-CeO}_2\text{-ZrO}_2$ and $\text{Cu(10\%)/TiO}_2\text{-CeO}_2\text{-ZrO}_2$. The representative peaks of Cu are found in 37° to 40° of 2θ (Habibi & Karimi 2014). In our materials, only a signal that overlaps the Cu signals is presented, so it is not possible to distinguish it clearly. (Najafi Nobar 2018).

The peaks representing the mixed oxide $\text{TiO}_2\text{-CeO}_2\text{-ZrO}_2$ are not observed in a defined way since only the micro-peaks are seen, but something is observed in the locations where each of the oxides is represented by making a single peak, this may be due to the fact that the oxides are in a single network and thus the existence of some crystalline phase cannot be appreciated in the diffraction patterns. (Ghodsí *et al.* 2008).

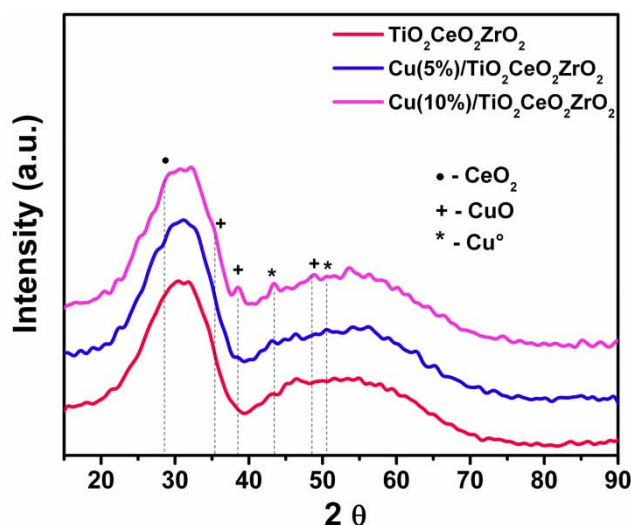


Figure 5 | XRD patterns of materials.

2-Chlorophenol degradation by catalytic wet oxidation

The reaction was carried out in a 600 ml Parr (batch) reactor, which contained 150 ml of an aqueous solution of 1,000 ppm of phenol at a temperature of 160°C , the partial pressure of oxygen of 15 bar and 150 mg of catalyst (1 g/L). The reaction was analyzed during a reaction time of 3 hours, to take samples at certain times.

The results indicate (see Figure 6) the differences between the copper-free material and the copper-containing materials. The material composed of the mixed oxides $\text{TiO}_2\text{-CeO}_2\text{-ZrO}_2$ has a low degradation percentage of

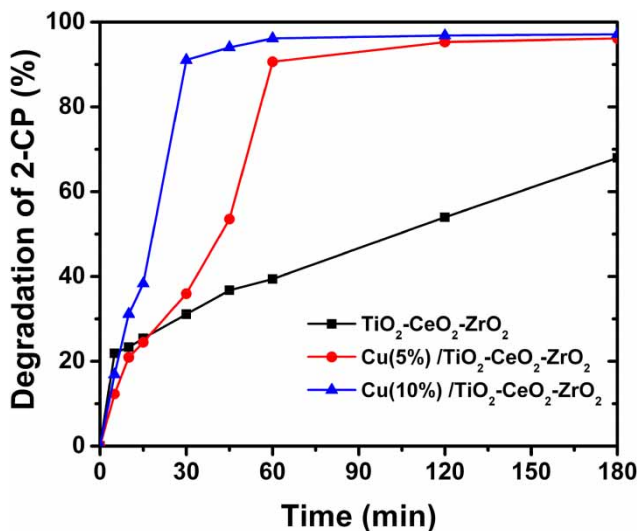


Figure 6 | 2-Cp conversion (%) by CWAOX at 160°C and 15 bar.

67.97%, after 3 hours of reaction, as is seen in Figure 6. In the case of materials containing 5% and 10% of copper, the 2-Cp degradation increases to 96.13% and 97.03% respectively, demonstrating that the active copper sites augment the 2-Cp degradation efficiency in the reaction of CWAO.

Total organic carbon analysis (TOC)

Figure 7 shows the behaviour of the Total Organic Carbon abatement (% Δ TOC); in this case, the effect of the Cu concentration in the reactions using the synthesized materials is strongly appreciated.

The results of conversion of 2-Cp (2-chlorophenol), TOC abatement (% Δ TOC) and CO_2 selectivity showed that the material without Cu is not efficient in the mineralization, as seen in Table 3, since it has the lowest carbon

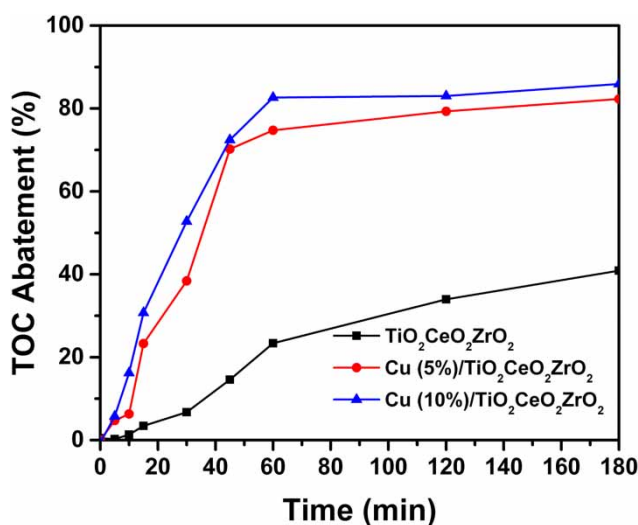


Figure 7 | Total Organic Carbon (TOC) abatement (% Δ TOC) of the 2-chlorophenol reaction of by CWAO at 160 °C and 15 bar.

Table 3 | Conversion of 2-Cp (2-chlorophenol), TOC abatement (% Δ TOC), CO_2 and carboxylic acids selectivity after 3 h of reaction at 160 °C and 15 bar of oxygen pressure

Analysis of the samples at the end of the reaction					
Catalyst	% Conversion		% Δ TOC	% SCO_2	% $\text{S}_{(\text{carboxylic acids})}$
	% Cu	of 2-Cp			
$\text{TiO}_2\text{-CeO}_2\text{-ZrO}_2$	0	67.97	44.90	66.05	33.95
Cu (5%)/ $\text{TiO}_2\text{-CeO}_2\text{-ZrO}_2$	5	96.13	82.53	85.85	14.15
Cu (10%)/ $\text{TiO}_2\text{-CeO}_2\text{-ZrO}_2$	10	97.03	89.10	91.82	8.18

abatement in respect to the other two materials containing Cu, of 44.90% Δ TOC and 66.05% SCO_2 although it has a good oxygen promoter due to the interaction with the Ce, which is not sufficient to achieve a high mineralization efficiency (SCO_2). The material with Cu at 10% reached a percentage of 89.01% Δ TOC and 91.82% SCO_2 being the one with the highest mineralization while the catalyst at 5% Cu presents 82.53% Δ TOC and 85.85% SCO_2 being lower than the increase presented by the 10% Cu.

Intermediates by-product study

The intermediate by-products were identified using a Shimadzu Prominence HPLC Chromatograph equipped with a Column Bio-Rad model Aminex HPX-87 fabricated of stainless steel and with the following measures: 300 mm height and 7.8 mm internal diameter, with a refractive index detector (RID-10A).

Only the intermediates by-products of maleic, oxalic and formic acids were detected. In previous works, these intermediates were detected to CWAO of phenol in batch FBR reactors using $\text{AgAu/ZrO}_2\text{-CeO}_2$ catalysts (Silahua-Pavón *et al.* 2019b) and $\text{RuAu/ZrO}_2\text{-CeO}_2$ catalysts (Izquierdo-Colorado *et al.* 2019). In accord to the pathway proposed by (Tu *et al.* 2014) it is proposed that the formation of intermediates formed at the beginning of the reaction as chlorohydroquinone, 4-chlororesorcinol, catechol and hydroquinone, are formed quickly and immediately they are transformed in maleic, oxalic and formic acids, which explains the high selectivity to CO_2 when Cu is added to the support (see Figure 8 and Table 3 for carbon balance). It is important to note that the pH of the medium decreased from the moment the first reaction sample was taken until the end of the reaction, which explains the formation of hydrochloric acid and carboxylic acids (maleic, oxalic and formic).

DISCUSSION

With regard to the specific area of the materials, when 5% Cu is added to the surface of the support, the specific area decreases from 291 m^2/g to 203 m^2/g and as the copper concentration increases, an increase in the specific area is generated up to 220 m^2/g , for this behaviour. It can be concluded that the sol-gel method has proved to be an effective method in the synthesis of mixed oxides since it provides a high surface area suitable to use it in advanced oxidation reactions such as CWAO. Moreover, incorporating Ce to

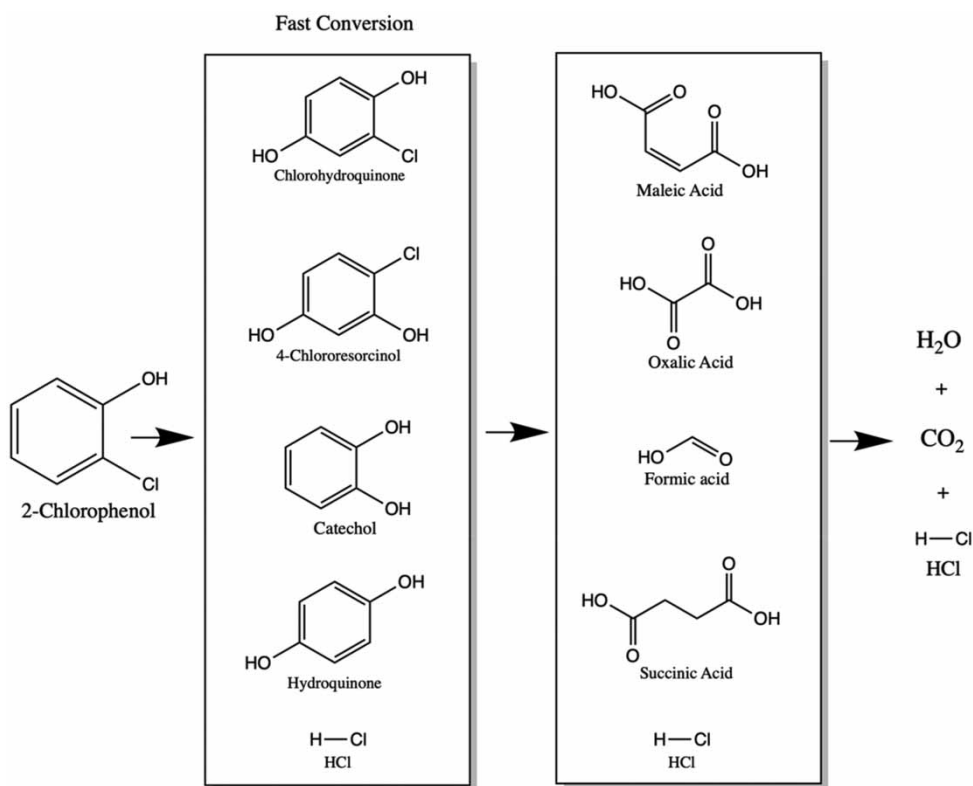


Figure 8 | Reaction pathway of catalytic wet air oxidation of 2-chlorophenol over $\text{Cu}/\text{TiO}_2\text{-CeO}_2\text{-ZrO}_2$ catalysts.

the materials, together with TiO_2 and ZrO_2 , provides structural properties that improve the specific surface area, and increases the electronic properties as observed by UV-Vis where the characteristics of Ce^{3+} and Ce^{4+} were identified. CWAOX reactions can be carried out because of the faculty that cerium has for transporting oxygen and going from Ce^{3+} to Ce^{4+} (Fu & Kyzas 2014; Vega-Garita *et al.* 2014). Cu can be identified in each of the different characterizations that were made to the catalysts, the increase of this element in the materials improved the activity and mineralization of the CWAOX of 2-cp; despite the decrease in the calculated theoretical percentage observed by SEM-EDS, the reaction results were satisfactory (Liu *et al.* 2017).

In the process of CWAOX, the results showed that the addition of Cu promotes a greater degradation in the reaction, as well as greater mineralization. Cu at 10% presents a slight increase in the conversion and mineralization of 2-Cp, this is due to a combination of Cu and the presence of Ce^{4+} and Ce^{3+} providing oxygen to the reaction and an increase in efficiency. Furthermore, after 45 minutes of reaction, a very visible increment is seen in the degradation and mineralization of 2-Cp, as a result of the presence of metal (Gao *et al.* 2018). The coexistence of the Ce^{4+} and Ce^{3+}

with Cu^{2+} and Cu^+ improves the CWAOX of 2-Cp. Ce^{4+} and Cu^{2+} co-exist with Ce^{3+} and Cu^+ . Ce^{3+} and Cu^+ are the main active sites where the reactants' molecules get adsorbed (Anushree *et al.* 2017). The reactant molecules are oxidized by the surface lattice oxygen, generating the oxygen vacancy. The free oxygen molecules in reactant gas would be easily trapped and released by these oxygen vacancies via the interaction between $\text{Ce}^{4+}/\text{Ce}^{3+}$ and $\text{Cu}^{2+}/\text{Cu}^+$. In other words, a synergistic effect is caused by metal and support (Yilmaz & Soylak 2017; Yilmaz *et al.* 2018). It's important to remark that acidity was studied in our group of research in the case of phenol (Monteros *et al.* 2015) and MTBE (Cervantes *et al.* 2013) by CWAOX. In the case of phenol, we concluded that the reaction takes place by catechol formation and subsequently organic acids and CO_2 (Oliviero *et al.* 2000) due to the Lewis acid sites, which can activate the electronic doublet of oxygen of hydroxyl function and thus enhance the ortho-oxidation of phenol. In this case, all catalysts showed a good selectivity to CO_2 related to the acid sites measured by $\text{ZrO}_2\text{-TiO}_2$ mixed oxides (Atanda *et al.* 2015; Silahua-Pavón *et al.* 2019a), which have a great quantity of Lewis sites related to Zr^{4+} and founded in this case in the UV-Vis analysis

(see Figure 4), as the quantity of Ce is relatively low, we can conclude that the acid sites are too a high value and that additionally, the HCl formation from 2-Cp improves the condition necessary to follow the route of the catechol and not the route of the hydroquinone formation. Another important contribution by our group was that if the route takes place by the formation of the quinones, the polymerization on the surface of the catalysts is important, therefore the deactivation of the material can be carried out due to the blocking of the superficial active sites (Hosokawa *et al.* 2003). The Ce loading effect, in this case, was important to enhance the CO₂ selectivity as explained by several authors (Hosokawa *et al.* 2003, 2005; Cuauhtemoc *et al.* 2009; Cervantes *et al.* 2013; Monteros *et al.* 2015; Rocha *et al.* 2015) by the formation of Ce⁴⁺-O²⁻-M that could favour the oxygen transfer between the catalyst surface and the adsorbed species by a redox mechanism. It's important to remark that the excess of Ce loading (≥ 50 wt%) increases the Oxygen Capacity Storage (OSC), which improves the para-oxidation of phenol entraining the carbon deposit by formation of polymer from *p*-benzoquinone (Monteros *et al.* 2015) and consequently the number of Lewis sites decrease too. It was found too by our group that the number of total sites increase for the mono and bimetallic catalysts by Ce loading of 10 wt% and decrease when the Ce loading attains 20 wt% (Izquierdo-Colorado *et al.* 2019) in RuAu/ZrO₂-CeO₂ catalysts. In this work, the quantity of Ce was only 5 wt%, which explains the high selectivity to CO₂ of the catalysts used in this study. In accordance with the above, in Figure 8 we propose a reaction pathway of 2-Cp in the CWAox using Cu/TiO₂-CeO₂-ZrO₂ catalysts.

CONCLUSIONS

TiO₂-CeO₂-ZrO₂ was used as a support to impregnate Cu at different amounts and to use it as a catalyst in the CWAox of 2-cp. This support shows a high surface area, with a heterogeneous morphology, without showing any well-defined crystal structure; besides, the interaction between these oxides improves their electronic properties. The increment in the amount of Cu in the support increases the surface area consequently this favours the contact surface in the catalytic evaluation. In the catalysts, Ce³⁺ and Cu⁺ are the main active sites that act as an oxygen promoter in the CWAox reaction, where the reactant molecules are adsorbed, this describes a synergistic effect between metal and support. The support showed a good activity with a SCO₂ higher than 50% in the CWAox of 2-Cp due to the

presence of Ce, which acts as an oxygen promoter in the material. The incorporation of copper improves the catalytic behaviour in the reaction and when the amount of this metal increases by up to 10%, the SCO₂ shows the highest value. Finally, a reaction pathway of 2-Cp is proposed in the CWAox using Cu/TiO₂-CeO₂-ZrO₂ catalysts.

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