THERMAL STABILITY OF THE Cu-CeO₂ INTERFACE ON SILICA AND ALUMINA, AND ITS RELATION WITH ACTIVITY IN THE OXIDATION REACTION OF CO AND THE DECOMPOSITION OF N₂O

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ABSTRACT

The effect of the support on the formation of the Cu-CeO₂ interface and its thermal stability after calcination at 500, 700 and 900 °C is studied. The supports used are SiO₂, because of its inert character, and Al₂O₃, because it can interact with the Cu and Ce species on the surface. The catalysts were characterized by BET, XRD, UV-vis DRS, and TPR with H₂. The catalytic activity in the CO oxidation reactions with O₂ at low temperature and the decomposition of N₂O were selected to visualize the effect of temperature on the concentration of Cu-CeO₂ interfacial sites. The results show that at a calcination temperature of 500 °C the formation of the Cu-CeO₂ interface is favored over the SiO₂ support. However, the stability of the Cu-CeO₂ interface on SiO₂ is much lower than on Al₂O₃, causing a substantial decrease of the interfacial sites calcining at 700 °C, and segregation of the Cu and Ce species on the surface of the silica, with complete loss of the catalytic activity in both reactions when calcining at 900 °C. In contrast, on alumina the Cu-CeO₂ interface is more stable and presents a significant catalytic activity in both reactions, even when calcinating at 900 °C. The characterization results show that the sintering process of Cu species and CeO₂ particles is less on the alumina support due to the greater interaction of the Cu and Ce with this support.

KEYWORDS: Cu, Ce, silica, alumina, CO oxidation, N₂O decomposition.

1. INTRODUCTION

The CuO-CeO₂ system has shown excellent catalytic properties for a series of reactions including the oxidation of CO with O₂ [1, 2] and the WGS reaction between CO and H₂O, which produces H₂ and CO₂ [3]. Furthermore, in the oxidation of CO with O₂, the Cu-CeO₂ system has proven to be even more active than Pt supported catalysts [4]. The CuO-CeO₂ system is also very active and selective in its preferential oxidation of CO with O₂ in the presence of H₂ (PROX reaction), making it a very attractive system to generate H₂ with the high purity required by fuel cells [5].

In both reactions, the CO oxidation and the WGS, the Cu-CeO₂ interface sites play an important role in the activity of the catalyst. The facility of the Ce (III) - Ce (IV) redox cycle and the high mobility of oxygen in the crystal structure of CeO₂ are two important properties of CeO₂ [6]. As a result, this oxide is capable of reversibly "adsorbing" oxygen. The high activity of the CuO-CeO₂ system as part of the CO oxidation with O₂ is attributed to the strong interaction between the Cu particles and the CeO₂ phase. Martinez-Arias et al. [7] proposed that CO reacts with oxygen in the Cu-CeO₂ interface, even at room temperature to produce CO₂ resulting in Cu⁴⁺ and Ce⁷⁺ formation and leaving an oxygen vacancy in the interface. Another molecule of CO can be adsorbed on the Cu⁴⁺, which accounts for the observation of this species by IR during the reaction. Re-oxidation of the surface occurs by the adsorption of O₂ from the gas phase in a mechanism of the Mars Van Krevelen type. The limiting reaction step should be some of the stages of re-oxidation of the catalyst (migration and/or dissociation of oxygen). The controversy on the exact nature of the active sites, the oxidation state of copper, and the reaction mechanism continues [8-11], but what is clear is that the sites are located on the interface between Cu and Ce. Regarding the WGS reaction, the generation of oxygen vacancies in the interface has often been cited as the reason for the high activity of this system. Indeed, in the redox mechanism used to explain this reaction, it is proposed that the H₂O molecule adsorbs on an oxygen vacancy, where the abstraction of oxygen and the generation of H₂ takes place. Subsequently, the oxygen atom is removed by CO which is adsorbed on a neighboring Cu site in the interface, generating a new oxygen vacancy on the surface and allowing the catalytic cycle to continue [3, 12].

It was recently reported that the CuO-CeO₂ system is also a highly active component in the direct decomposition of N₂O into N₂ and O₂ [13-16]. This system generates a complete N₂O decomposition in a stream of 2500 ppm of N₂O at temperatures below 550 °C [16]. The abatement of N₂O is very important in controlling greenhouse gases, since it is known that, besides being a toxic gas, N₂O contributes heavily to the greenhouse effect [16]. One of the main sources of N₂O is the industrial production of nitric acid by ammonia oxidation [13]. There are different options for abating N₂O depending on where the catalytic process is performed. It has been found that the best choices for existing plants, are locating the catalyst just under the Pt metal gauze in the ammonia burner (process-gas option), or in the tail-gas train (tail-gas option) [13]. In the first option, the catalyst must be able to withstand high temperatures, near 850 °C, while in the latter, conditions and temperatures are more moderate and the catalyst must work at temperatures near 500 °C. Some commercial catalysts for the Cu-CeO₂ system in N₂O process-gas decomposition are: CuO/Al₂O₃ (BASF), LaₓCeₓCoO₃ (Johnson Matthey), Co₃AlO₆CeO₃ (Yara International), and Fe₃AlO₆ (PKR2-INS). Furthermore, U-Def EnviNOS® markets a tail-gas process for removing N₂O and NOx that uses iron-containing zeolites.

Considering the moderate temperature range that was studied in the CuO-CeO₂ system (ambient to 700 °C) [15, 16, 13], in principle, these catalysts could be used in a tail-gas process. The high activity of the CuO-CeO₂ system in N₂O decomposition was attributed to the existence of oxygen vacancies in the interface of the Cu-Ce sites that stabilize Cu⁺, which is responsible for the abstraction of the oxygen atom from the N₂O molecule [14].

As shown in all these reactions, as well as other reactions catalysed by the CuO-CeO₂ system, the formation of the Cu-CeO₂ interface is essential for obtaining a catalytically active system. In many cases, the Cu-CeO₂ system is formed either by co-precipitating the precursors of both metals or by using a method that leads to the formation of mixed oxides [14, 15] or by supporting Cu on previously formed CeO₂ [15, 16]. Indeed, all reports that discuss the activity of the CuO-CeO₂ system in decomposing N₂O [13-16], use Cu catalysts that are supported on CeO₂ or use mixed oxides prepared by coprecipitation. A disadvantage to these catalysts is that they are produced with specific areas below 100 m²/g [18], and most often, even less areas of less than 50 m²/g [19, 20], unless special methods of preparation are used, such as a reversed micro emulsion method [8] in which the mixed oxide reaches areas between 130 and 150 m²/g after calcination at 500 °C. Furthermore, the specific surface area of these catalysts decreases strongly with increasing calcination temperature. Djinovic et al. [21] show that the specific surface area of a CuO/CeO₂ catalyst decreases from 40.2 m²/g (at 450 °C), to only 8.3 m²/g after calcining at 550 °C. With the goal of improving the thermal stability of CeO₂, the addition of some dopants such as ZrO₂ or La₂O₃ to the cerium oxide has been explored [22, 23]. Alternatively, the CuO-CeO₂ system could be supported on a third oxide with high specific surface area and high thermal stability, with the added advantage that the catalyst acquires the mechanical properties of the support [24]. Regardless of the reason for using a third oxide for support, it is important for the Cu and CeO₂ to interact on the support’s surface forming a Cu-CeO₂ interface with a high interfacial area.

In our laboratory, in recent years we have conducted a series of studies using monometallic CuO catalysts and bimetallic CuO-CeO₂ catalysts supported on different oxides that are commonly used as supports: SiO₂, Al₂O₃, and ZrO₂ [25]. Reactions in which these catalysts have been tested include the CO oxidation with O₂ and the WGS reaction.

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In the oxidation reaction of CO with O₂ on a Cu supported monometallic catalyst, the support plays an important role in the activity of the catalysts as shown by the significantly greater activity generated by zirconium oxide catalysts compared to that seen with SiO₂ and Al₂O₃ supports [25]. Regardless of the support used, the addition of CeO₂ generates bimetallic catalysts that are much more active than the monometallic ones. This increase in activity is due to the formation of the Cu-CeO₂ interface on the support’s surface, as indicated by various catalyst characterization techniques [25, 26]. However, the formation of the Cu-CeO₂ interface does not occur in the same way on all supports. In fact, when using SiO₂ as support, Cu-CeO₂ generates a more active interface, while the Al₂O₃ support generates a less active interface. This was attributed to the inert character of the silica, which promotes the formation of an interface similar to that formed by supporting Cu directly on CeO₂.

While the inert character of the silica seems to be favorable for the formation of a Cu-CeO₂ interface that is highly active in the oxidation of CO with O₂ and in the WGS reactions, insensitivity can generate a problem with the stability of this interface at high temperatures. Indeed, if a catalyst with 2% Cu and 8% Ce, prepared by coimpregnation of the nitrates of both metals on SiO₂ (Aerosil 200), is calcined at 500 ºC, a highly active catalyst for CO oxidation is obtained which has a practically 100% conversion rate below 180 ºC. However, if the calcination temperature is increased to 650 ºC or higher temperatures, a marked decrease in catalytic activity occurs, falling below 140 for CO oxidation is obtained on 2% Cu and 8% Ce, prepared by coimpregnation of the nitrates of both metals on SiO₂ (Aerosil 200), is calcined at 500 ºC, a highly active catalyst for CO oxidation is obtained which has a practically 100% conversion rate below 180 ºC. However, if the calcination temperature is increased to 650 ºC or higher temperatures, a marked decrease in catalytic activity occurs, falling below 140 ºC.

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3.- RESULTS

3.1 Characterization of the catalysts

Table 1 shows the BET area of the different mono- and bimetallic catalysts. In the case of the SiO₂ support, increasing the calcination temperature from 500 to 900 ºC has little effect on the specific surface area of the catalysts, as expected from the high thermal stability of silica. In the case of the monometallic Cu catalysts, the specific surface area decreases from 130 to 110 m²/g when calcining between 500 and 900 ºC, while in the bimetallic Cu-Ce catalysts the specific surface area decreases from 128 to 104 m²/g over the same calcination temperature range.

In the case of the Al₂O₃ support, in the monometallic Cu as well as in the bimetallic Cu-Ce catalysts, increasing the calcination temperature of the catalyst has some effect on the specific surface area between 500 ºC and 700 ºC. In the case of the monometallic Cu catalysts, the area varies between 130 and 111 m²/g when calcining between 500 and 700 ºC, while with the bimetallic catalysts the area decreases from 109 to 96 m²/g for the same temperature range. However, with calcining at 900 ºC, the specific surface area of the mono- and bimetallic catalysts decreases to around 60 m²/g, showing the lower thermal stability of alumina.

Table 1. BET specific surface area and H₂ consumption of the various monometallic and bimetallic catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET Surface Area (m²/g)</th>
<th>Ratio of: H₂ consumed / H₂ required for complete reduction of CuO</th>
<th>CeO₂ particle diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Monometalic</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu/Si-500</td>
<td>130</td>
<td>0.99</td>
<td></td>
</tr>
<tr>
<td>Cu/Si-700</td>
<td>120</td>
<td>1.01</td>
<td></td>
</tr>
<tr>
<td>Cu/Si-900</td>
<td>110</td>
<td>1.02</td>
<td></td>
</tr>
<tr>
<td>Cu/Al-500</td>
<td>130</td>
<td>0.82</td>
<td></td>
</tr>
<tr>
<td>Cu/Al-700</td>
<td>111</td>
<td>0.60</td>
<td></td>
</tr>
<tr>
<td>Cu/Al-900</td>
<td>60</td>
<td>0.59</td>
<td></td>
</tr>
<tr>
<td><strong>Bimetallic</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuCe/Si-500</td>
<td>128</td>
<td>1.33</td>
<td>6.0</td>
</tr>
<tr>
<td>CuCe/Si-700</td>
<td>128</td>
<td>1.08</td>
<td>8.6</td>
</tr>
<tr>
<td>CuCe/Si-900</td>
<td>104</td>
<td>0.99</td>
<td>12.0</td>
</tr>
<tr>
<td>CuCe/Al-500</td>
<td>109</td>
<td>1.04</td>
<td>5.7</td>
</tr>
<tr>
<td>CuCe/Al-700</td>
<td>96</td>
<td>0.69</td>
<td>6.3</td>
</tr>
<tr>
<td>CuCe/Al-900</td>
<td>58</td>
<td>0.64</td>
<td>7.1</td>
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</table>

The effect of the calcination temperature on the crystal structure of CuCe/Al-900.
the catalysts supported on SiO$_2$ is shown in Figure 1A. In the case of the monometallic catalysts, the peaks of the tenorite structure of CuO at 2$\theta$ = 35.5$^\circ$ and 38.2$^\circ$ are seen clearly in all the catalysts calcined between 500 $^\circ$C and 900 $^\circ$C: Cu/Si-500, Cu/Si-700 and Cu/Si-900. These results confirm what has been reported previously [25, 26], and show that Cu forms crystalline CuO particles on silica, even at low calcination temperatures (500 $^\circ$C). In contrast, in the diffractograms of the bimetallic Cu-Ce catalysts, the CuO peaks are no longer seen in the catalysts calcined at 500 $^\circ$C (CuCe/Si-500) and 700 $^\circ$C (CuCe/Si-700), and they can only be seen weakly in the bimetallic catalyst calcined at 900 $^\circ$C (CuCe/Si-900). The effect of the increased dispersion of Cu by adding CeO$_2$ has been reported in the literature [25, 26, 29], so it is not strange for the CuO peaks to disappear in the bimetallic catalysts calcined at 500 $^\circ$C and 700 $^\circ$C.

Regardless of the calcination temperature, the peaks corresponding to CuO or crystalline CuAl$_2$O$_4$ are not found in any of the catalysts. The classic studies of Friedman et al. [27] and Stromehier et al. [28] show that at low loads the Cu enters the defect spinel of the $\gamma$-alumina support to yield a well dispersed phase which is not detected by X-ray diffraction [27,28]. This Cu structure is usually cited as “copper aluminate surface phase” because it “resembles” the CuAl$_2$O$_4$ phase. According to these authors, as long as the Cu load does not exceed 4%-5% for every 100 m$_2$/g, the appearance of CuO is not expected [27, 28]. Considering the above, it is not strange that in our catalysts the formation of crystalline CuO is not seen. On the other hand, the formation of Cu aluminate can be observed by XRD at greater Cu loads and higher calcination temperatures. In fact, Luo et al. [30] report the formation of Cu aluminate in catalysts with 11% or higher loads at temperatures above 800 $^\circ$C. Because of this, no copper aluminate is expected in our catalysts. In the case of the bimetallic Cu-CE catalysts, CeO$_2$ peaks are seen at 2$\theta$ = 28.6, 33.1, 47.6, and 56.4$^\circ$. As reported in Table 1, although the size of the CeO$_2$ crystal increases from 5.7 nm at 500 $^\circ$C to 7.1 nm at 900 $^\circ$C, this increase is noticeably less than that observed in the catalysts supported on silica. It is clear, therefore, that the greater interaction of the CeO$_2$ particles with alumina decreases the degree of sintering with the temperature increase. The peaks corresponding to crystalline CuO are not detected by XRD in any of the catalysts, regardless of the calcination temperature, for the reasons already discussed for the monometallic catalysts supported on alumina.

The results of the temperature programmed reduction (TPR) experiments using H$_2$ as reductant are shown in Figure 2A for silica supported catalysts, and Figure 2B for alumina supported catalysts.

In the case of the monometallic catalysts supported on SiO$_2$, there is only one reduction peak, with a maximum that is displaced from 290 $^\circ$C to 308 $^\circ$C by calcining between 500 and 900 $^\circ$C (Figure 2A). This peak has been seen in previous work by our group [25], and, according to the literature, it can be associated with bulk CuO [31-33]. The assignment of this peak to bulk CuO agrees with what has been observed in the XRD diffractograms, which show clearly the formation of crystalline CuO in all the monometallic Cu catalysts supported on silica. Table 1 reports the consumption of H$_2$ by the different catalysts, expressed as the ratio between the consumed H$_2$ and the H$_2$ required to reduce all the Cu$^{2+}$ to Cu$.^{0}$. All the fractions are very close to 1.0, indicating that the reduction of the Cu oxide to metallic Cu is complete in the temperature range used in the TPR experiments.

In the case of the bimetallic catalysts, with the catalysts calcined at 500 $^\circ$C (CuCe/Si-500), the reduction occurs at a considerably lower temperature than with the monometallic catalysts. In effect, two reduction peaks are seen with maxima at 195 and 214 $^\circ$C. The appearance of two reduction peaks agrees with what was seen in previous work [25, 26]. According to the literature the first peak is associated with the reduction of highly dispersed Cu species in contact with CeO$_2$, and the second peak with the reduction of Cu particles (clusters), but also in contact with CeO$_2$. On the other hand, as shown in Table 1, the ratio of the consumption of H$_2$ is greater than 1, indicating that another species is being reduced together with Cu species. The literature reports that at Cu loads above 380 $^\circ$C, but when Cu interacts with the CeO$_2$ CeO$_2$ is reduced together with the Cu [4, 25, 34], therefore accounting for a ratio greater than 1. Therefore, the result shown in Table 1 (ratio = 1.33) confirms the idea that the Cu species are interacting strongly with CeO$_2$ in the catalysts calcined at 500 $^\circ$C. As the calcination temperature is increased to 700 $^\circ$C, only one maximum is seen around 265 $^\circ$C, which can be associated with larger Cu particles interacting with CeO$_2$. At the same time, the overconsumption of H$_2$ reported in Table 1 decreases strongly in this catalyst (ratio = 1.08), suggesting that the interaction between Cu and CeO$_2$ also decreases by calcining at 700 $^\circ$C.

Finally, calcining at 900 $^\circ$C a single peak is seen with a maximum at 308 $^\circ$C, which can be assigned to the reduction of bulk CuO particles that do not interact with CeO$_2$. In fact, this peak is located at practically the same temperature as the one seen in the monometallic catalyst. Again, this assignment agrees with the TPR results, which show the formation of crystalline CuO when calcining the bimetallic catalyst at 900 $^\circ$C. Furthermore, the results of the consumption of H$_2$ in Table 1 (ratio = 0.98) indicates that in this case there is practically no overconsumption of H$_2$, and therefore the only species that is reduced is CuO, reflecting the separation of the CuO and CeO$_2$ particles on the surface of the SiO$_2$ support when calcining at 900 $^\circ$C.

The H$_2$ consumption curves (TPR) of catalysts supported on alumina are shown in Figure 2B. In the case of “copper monometallic” catalyst calcined at 500 $^\circ$C (Cu/Al-500), there is a main reduction peak with a maximum at 280 $^\circ$C. The literature is somewhat contradictory in assigning this reduction peak. At low Cu loads, Dow et al. [35] report a single reduction peak associated with highly dispersed Cu at about 210 $^\circ$C, while the formation of bulk CuO occurs only at
Cu loads greater than 5%, generating a second peak with a maximum close to 245 °C. Yao et al. [36] also saw one reduction peak at low Cu loads, but with a maximum at 300 °C which they attributed to highly dispersed Cu, forming isolated and two- and three-dimensional small copper clusters. Xiaoyuan et al. [37] also found a single reduction peak with a maximum at 317 °C for a 1% Cu on alumina catalyst calcined at 500 °C for two hours. Therefore, considering the previous results and the failure to detect CuO in the XRD tests, this peak at 280 °C may be associated with highly dispersed Cu. On the other hand, Table 1 shows that the consumption of H₂ is lower than that necessary for reducing all the CuO present in the catalyst (ratio = 0.82), in agreement with previous studies [38].

CuAlO₂ supports calcined at 500 °C, 700 °C and 900 °C. (A) Supported on SiO₂, (B) Supported on Al₂O₃. Operation conditions: flow rate = 20 cm³/min of 5%H₂, balance in He; heating rate = 10 °C/min; catalyst mass = 100 mg.

When the calcination temperature is increased to 700 °C (Cu/Al-700), the reduction maximum is displaced to 315 °C, and H₂ consumption ratio decreases to 0.60, indicating that the Cu is harder to reduce than when calcining at 500 °C. It is frequently found in the literature that increasing the calcination temperature leads to the displacement of the reduction peak to lower temperatures. In fact, Luo et al. [30] and Yahiro et al. [39] show that the reduction peaks are displaced to lower temperatures by calcining between 500 and 700 °C. However, in these cases the high Cu load, 12% in the case of Luo et al. and 33% in the case of Yahiro et al., lead to the formation of CuO, so the displacement to lower temperatures is interpreted by these authors as an increased reduction ease of CuO due to a redispersion of this species. In our case no bulk CuO is formed, so the displacement of the reduction peak to higher temperature by calcining at 700 °C must be explained by the formation of a Cu species that interacts to a greater degree with the alumina, hindering its reduction. Something similar was reported by Dumas et al. [40], who found that calcining a catalyst with 10% Cu at 600 to 750 °C, a simultaneous displacement of the highly dispersed Cu peak from 242 °C to 300 °C took place, while the bulk CuO peak was displaced from 312 to 300 °C, forming a single reduction peak with a maximum at 300 °C. In other words, calcination at 700 °C can generate the formation of less reducible species from highly dispersed Cu, at the same time generating more easily reducible species from bulk CuO.

Finally, when the calcination temperature is increased to 900 °C (Cu/Al-900), the ease of reduction of Cu increases again, and the maximum is displaced to a lower temperature, very close to the one observed for the catalyst calcined at 500 °C. In the literature it is reported that calcination at 900 °C causes the formation of bulk CuAlO₂ [28], so this reduction peak may be associated with this species. However, the reduction maximum temperature observed with our catalyst is significantly lower than that reported in the literature for the bulk CuAlO₂ species. In fact, Severino et al. [38] report that the CuAlO₂ reduction peak is at 445 °C, while Yahiro et al. [39] find the maximum at 410 °C, and Sato et al. [41] report the reduction of Cu aluminate with a maximum at 450 °C. On the other hand, and because of the low Cu load, our XRD analyses do not allow the formation of Cu aluminate to be discarded. Therefore, it is only possible to speculate that the peak at 280 °C corresponds to the reduction of highly dispersed Cu species. Table 1 shows, however, that H₂ consumption (ratio = 0.59) is less than when calcining at 500 °C, so the concentration of reducible Cu species decreases significantly by calcining between 500 and 900 °C. The addition of CeO₂ produces important changes in the reduction curves with H₂ of the catalysts supported on alumina. The bimetallic catalyst calcined at 500 °C shows two reduction peaks with reduction temperature maxima between 220 and 250 °C attributed to Cu species of different sizes interacting with CeO₂, as discussed previously by our group [see ref. 25 and work cited therein], H₂ consumption with this catalyst, which is reported in Table 1, is also greater than in the monometallic catalyst calcined at the same temperature, confirming the formation of the Cu-CeO₂ interface. Increasing the calcination temperature to 700 °C, the maximum of the first peak remains practically unshifted, but there is a shift of the second reduction peak’s maximum from 250 to 290 °C. However, the reduction maxima are lower than the maximum presented by the Cu monometallic catalyst calcined at 700 °C, reflecting that the Cu-CeO₂ interaction has not disappeared completely in the catalyst calcined at 700 °C. Calcining at 900 °C results in a decrease of the area under the lower temperature peak, but it is clearly seen as a shoulder at 230 °C. In a manner similar to what happens with the monometallic catalyst, the maximum of the higher temperature peak shifts to a reduction temperature lower than that found upon calcining at 700 °C. The maximum is displaced from 290 to 270 °C, a temperature 10 °C lower than that found with the monometallic catalyst, suggesting that there still is an interaction with CeO₂. Table 1 shows that there is a slightly greater H₂ consumption than in the Cu monometallic catalyst calcined at the same temperature. Both observations lead to the conclusion that there still are sites corresponding to the Cu-CeO₂ interface in the catalyst calcined at 900 °C.

The UV-vis DRS spectrum of the monometallic and bimetallic catalysts supported on SiO₂ is shown in Figure 3A. In the case of monometallic catalysts, the spectrum is dominated by a wide absorption band with a maximum at 660 nm. According to the literature, this band can be assigned to d-d transitions of Cu²⁺ in bulk CuO [42, 43]. In fact, Gang et al. [42] see this band clearly in unsupported CuO. The adsorption edge characteristic of bulk CuO particles is also clearly seen at wavelengths longer than 750-800 nm [44]. Therefore, the UV-vis DRS spectra are in perfect agreement with what is seen in the XRD and the TPR observations, which show the formation of bulk CuO in these catalysts regardless of the calcination temperature. On the other hand, the spectra of the bimetallic catalysts are dominated by the absorption band of cerium oxide. In fact, below 400 nm, the absorption band corresponding to Ce⁴⁺—oxygen charge transfer transitions [45] is seen clearly, with a maximum close to 290 nm for the catalyst calcined at 500 °C, which does not change significantly as the calcination temperature is increased. The zone above 400 nm is where the largest changes occur as the calcination temperature is increased. The band corresponding to CuO bulk species supported on SiO₂ becomes more intense as the calcination temperature is increased between 500 and 700 °C, and it is clearly observable in the catalyst calcined at 900 °C. Again, this result agrees with the phase separation between CuO and CeO₂, which was inferred from the XRD and TPR analyses.
2-Cu species, or, possibly, cluster-
3-O UV-vis DRS spectra of monometallic (Cu) and bimetallic
2+ 2-
4+ 2
3-ligand-to-metal charge transfer [43], and a wide
2-
2+ oxygen charge transfer transitions, and the
2+
2+ catalyst calcined at 500 ºC (Cu/Al-500) is very similar to those reported
bimetallic catalysts supported on alumina. The spectrum of the monometallic
2+ 2-
2 (CuCe) catalysts calcined at 500 °C, 700 °C and 900 °C. (A) Supported on

Figure 3B shows the UV-vis DRS spectra of the monometallic and
2-
3.2 Catalytic activity
The conversion of CO as a function of reaction temperature for the
monometallic Cu catalysts and the bimetallic Cu-Co catalysts supported on
SiO 
2-
3. Catalysts calcined at 500 °C, which presents a 7% conversion at 220 ºC, the monometallic
catalysts calcined at 700 and 900 ºC are practically inactive in the temperature
range used in this study. The XRD analysis, the TPR experiments, and the UV-
vis DRS tests show that the Cu is found forming bulk CuO on the silica surface,
a species that has low activity in the oxidation of CO [25, 38]. Adding CeO 
2-
The activity of the catalyst calcined at 500 °C increases considerably, reaching
almost 100% conversion at 120 ºC, as shown in Figure 4A. The great activity
increase observed in the bimetallic catalyst confirms what has been reported
extensively in the literature, that the sites of the Cu-CoO interphase have a
very high activity in this reaction [1-7]. In fact, the TPR experiments show that
there is a strong interaction between the Cu and Ce species on the surface of this
catalyst. As calcination temperature is increased to 700 ºC, the activity drops
considerably, in agreement with the decrease of the Cu-CoO interactions, due
mainly to the increase of the cerium oxide particle size reported in Table 1. It
is interesting to note that in our previous paper [26], calcination at that same
temperature of a Cu-CoSiO 
2-
shape separation is associated not only with the large growth of the CeO 
2-
particles on the surface of the silica, but also with the formation of the CuO bulk phase. The UV-vis DRS analysis of this catalyst confirms also the appearance of bulk CuO particles in the
bimetallic catalyst calcined at 900 °C.
Figure 4B shows the activity of catalysts supported on alumina. The activity of the monometallic Cu catalysts supported on alumina is low, but, in contrast with the catalysts supported on silica, the catalyst calcined at 900 ºC shows some activity. The catalyst calcined at 900 ºC has an activity slightly higher than that of the catalyst calcined at 700 ºC. This result, which seems unexpected, is in agreement with the greater facility of reduction of the catalyst calcined at 900 ºC, compared to the one calcined at 700 ºC, which was observed in the TPR experiments. This is a point that deserves more attention in future work. As expected, the addition of CeO 
2-
produces a strong increase of the activity of the catalysts. Obviously, the formation of interfacial Cu-CoO sites on the surface of alumina explains this activity increase.

Figure 3: UV-vis DRS spectra of monometallic (Cu) and bimetallic
(Cu-Co) catalysts calcined at 500 °C, 700 °C and 900 °C. (A) Supported on
SiO 
2-
(B) Supported on Al$_2$O$_3$.

Figure 3B shows the UV-vis DRS spectra of the monometallic and
bimetallic catalysts supported on alumina. The spectrum of the monometallic
catalyst calcined at 500 °C (Cu/Al-500) is very similar to those reported
previously in the literature for the CuO/Al$_2$O$_3$ system [42, 46]. It is characterized
by a band below 400 nm, with a maximum close to 240 nm that has been
attributed to an O$^-$ $\rightarrow$ Cu$^{2+}$ ligand-to-metal charge transfer [43], and a wide
band with a maximum around 740 nm attributed to d-d transitions of Cu$^{2+}$
with octahedral symmetry. It is important to point out that the adsorption edge
characteristic of bulk CuO particles, clearly observable in the monometallic
catalysts supported on SiO$_2$ is not seen in any of the catalysts supported on
alumina. This is consistent with expectations, in view of the high dispersion
of the Cu on this support observed by XRD. Calcining at a higher temperature
does not result in major changes in the spectrum, except a widening of the band
between 300 and 400 nm in the catalyst calcined at 900 °C. This widening may
be due to charge transfer involving Cu$^{2+}$-O$^-$-Cu$^{2+}$ species, or, possibly, cluster-
like species [47]. In the spectrum of the bimetallic catalyst calcined at 500 °C,
a large peak is seen in the low wavelength zone, with a maximum at 300 nm and
a shoulder at 240 nm. Considering what has been discussed previously, the
former may be associated with Ce$^{3+}$-oxygen charge transfer transitions, and the
latter to an O$^-$ $\rightarrow$ Cu$^{2+}$ ligand-to-metal charge transfer. Between 600 and 850
nm, the characteristic band of the d-d transitions of Cu$^{2+}$ are observed, and as in
the case of the CuO/Al$_2$O$_3$ catalysts, it is not possible to see the adsorption edge
characteristic of bulk CuO particles. Calcining at higher temperatures results
in no important changes in the positions of the maxima of the absorption bands
or signs of the adsorption edge of the bulk CuO particles. The above indicates
that, in contrast with what was seen for the bimetallic catalysts supported on
SiO$_2$, Cu retains a high dispersion even in the bimetallic catalyst calcined
at 900 °C. This result is in complete agreement with what was observed by
XRD, where the CuO crystalline species is absent in the catalysts supported on
alumina calcined between 500 and 900 °C.

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What is most interesting, however, is that calcination at high temperatures, even though it decreases the activity of the bimetallic catalysts supported on Al₂O₃, it does so in a smaller proportion than when they are supported on silica. In effect, when calcining at 900 ºC, the CuCe/Si-900 catalyst is completely inactive, while the CuCe/Al-900 catalyst shows considerable activity in the oxidation of CO, achieving 60% conversion at 220 ºC. This behavior coincides with what is seen in the TPR experiments, where the ease of reduction increases by calcining between 700 and 900 ºC. On the other hand, the addition of CeO₂ produces an increase in the activity of all the catalysts supported on alumina. This activity increase, due to adding CeO₂, is not as important as that observed when using SiO₂ for support, due to the activity of the monometallic Cu catalysts supported on alumina. The bimetallic catalyst calcined at 500 ºC achieves 95.4% conversion at 600 ºC, which is significantly greater than the 63.5 % achieved by the monometallic catalyst.

The results of the activity of the different monometallic and bimetallic catalysts supported on SiO₂ and Al₂O₃ in the decomposition of N₂O are shown in Figures 5A and 5B, respectively.

Figure 5A shows all the monometallic Cu catalysts supported on silica are inactive in the decomposition of N₂O. As expected, the addition of CeO₂ improves noticeably the activity of the catalysts, achieving more than 80% conversion with the catalyst calcined at 500 ºC. This result shows clearly that the Cu-CeO₂ interface is responsible for the catalytic activity of these systems, as already reported in the literature [13-16]. If the Cu-CeO₂ interface is responsible for the catalyst’s activity, it would be expected that the N₂O decomposition activity should follow the same trend as the oxidation activity of CO with O₂. In effect, this is what happens. With calcining at 700 ºC, the activity decreases substantially, and it is practically nil after calcining at 900 ºC, following the same trend as in the CO oxidation reaction. The decrease of the interfacial sites due to the sintering and segregation of Cu species and CeO₂ particles on the surface of the silica account for the behavior in the decomposition of N₂O.

When alumina is used for support, the behavior of the monometallic Cu catalysts is very different from that observed on Cu supported on silica. Figure 5B shows that the monometallic Cu catalysts have a noticeable catalytic activity in the decomposition of N₂O, which is consistent with other studies [36, 48], achieving 63.5% conversion at 600 ºC in the case of the catalyst calcined at 500ºC. Increasing the calcination temperature to 700 ºC, reduces the activity at 600 ºC to 48.1%, and calcining at 900 ºC increases it slightly, reaching 51.8% conversion. This behavior coincides with what is seen in the TPR experiments, where the ease of reduction increases by calcining between 700 and 900 ºC. On the other hand, the addition of CeO₂ produces an increase in the activity of all the catalysts supported on alumina. This activity increase, due to adding CeO₂, is not as important as that observed when using SiO₂ for support, due to the activity of the monometallic Cu catalysts supported on alumina. The bimetallic catalyst calcined at 500 ºC achieves 95.4% conversion at 600 ºC, which is significantly greater than the 63.5 % achieved by the monometallic catalyst.
When the bimetallic Cu-Ce catalyst supported on alumina is calcined at 700 °C (Figure 5B), the activity at 600 °C drops slightly to 86.5%. This is significantly lower than the 48.1% conversion activity of the monometallic catalyst calcined at the same temperature, demonstrating the importance of the activity of the Cu-CeO₂ interface. Increasing calcination temperature to 900 °C, the activity of the bimetallic Cu-Ce catalyst drops to 61.1%, and the difference with respect to the conversion of the monometallic Cu catalyst (48.1%) decreases. It is evident that calcination at 900 °C causes a decrease of the concentration of interface sites, but their concentration is still sufficiently high to keep an activity greater than that of the monometallic catalyst calcined at the same temperature.

In short, the results of the NO₂ decomposition activity confirm that the sites of the Cu-CeO₂ interface are highly active in this reaction and that the stability of this interface is better when it is supported on alumina rather than on silica. Therefore, the characterization of the catalysts as well as their activity in the oxidation of CO with O₂ and the decomposition of NO₂ reactions show that the thermal stability of the Cu-CeO₂ interface is better when using alumina for support, in the calcination temperature range of 500 °C to 900 °C used in the present study.

4.- CONCLUSIONS

The results clearly show that the support has an important influence on the formation and stability of the Cu-CeO₂ interface. Although the formation of interfacial Cu-CeO₂ sites is favored in the catalysts calcined at 500 °C using silica for support, the thermal stability of the interface is low. Calcination at 900 °C causes the growth of the Cu species and CeO₂ particles, and their complete separation on the surface of the silica. The disappearance of the Cu-CeO₂ interface sites is responsible for the catalytic activity in the oxidation of CO and the decomposition of NO₂. On the one hand, the inert character of silica improves the interaction between Cu and CeO₂, and the decomposition temperature is increased.

In contrast, if Al₂O₃ is used for support, the bimetallic catalysts maintain an important activity in both reactions when they are calcined at 900 °C, due to a greater stability of the Cu-CeO₂ interface. This stability is attributed to the interaction between Cu and CeO₂, to the structure of these species as the calcination temperature is increased.

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