

# CuO and CeO<sub>2</sub> catalysts supported on Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, and SiO<sub>2</sub> in the oxidation of CO at low temperature

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## ABSTRACT

The effect of the support, Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, and SiO<sub>2</sub>, on the activity for CO oxidation of a series of CuO and CeO<sub>2</sub> monometallic and bimetallic catalysts was studied. The catalysts were prepared by coimpregnation of the support with the adequate amount of Cu and Ce nitrates to obtain a loading of 2% Cu and/or 8% Ce. It was found that the support has a strong influence on the activity of the different bimetallic catalysts. Interestingly, the SiO<sub>2</sub> supported catalyst shows the higher activity. The bimetallic supported catalysts follow the activity sequence CuO–CeO<sub>2</sub>/SiO<sub>2</sub> > CuO–CeO<sub>2</sub>/ZrO<sub>2</sub> > CuO–CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>. In the absence of CeO<sub>2</sub>, the most active monometallic catalyst was the CuO/ZrO<sub>2</sub> system. The different degree of interaction between CuO and CeO<sub>2</sub> particles, induced by the support, can explain the activity results for the bimetallic catalysts.

## Keywords:

Al<sub>2</sub>O<sub>3</sub>  
SiO<sub>2</sub>  
ZrO<sub>2</sub>  
Copper  
CeO<sub>2</sub>  
CO oxidation

## 1. Introduction

The oxidation of CO to CO<sub>2</sub> is a very important reaction from the standpoint of environmental control. Although this reaction is traditionally carried out on supported noble metals, it has been well known for many years that transition metals, particularly Cu, are also very good catalysts for it [1].

In recent years, and moved by the need to remove CO from the feed stream of fuel cells, there has been renewed interest in this reaction, and numerous papers have been published on the selective oxidation of CO with O<sub>2</sub> in the presence of large amounts of H<sub>2</sub> (PROX reaction). Different catalytic systems have been studied for this reaction, among them those based on noble metals [2–6], Au [7–10], and transition metals, especially copper-based catalysts [11–22]. The greater activity of Cu compared to that of other transition metals like Co, Ni, Cr, and Zn has been reported recently by Mariño et al. [15], confirming that it is one of the best candidates for replacing the noble metals.

The most widely studied catalysts based on copper for the PROX reaction include CeO<sub>2</sub> as a component, and can be classified into three kinds: (i) CuO and CeO<sub>2</sub> catalysts [11–16], (ii) CuO catalysts doped with CeO<sub>2</sub> (or vice versa) supported on alumina [17–20],

and (iii) CuO catalysts supported on mixed Ce<sub>x</sub>Zr<sub>(1-x)</sub>O<sub>2</sub> oxides [21,22].

It is well known that the CuO–CeO<sub>2</sub> system has excellent activity in the oxidation of CO [23], even higher than that of the noble metals [24], so it is not strange that a large part of the publications on the PROX reaction are related to the CuO–CeO<sub>2</sub> system. The ease of the Ce(III)–Ce(IV) redox cycle and the high mobility of oxygen in the crystal structure are two important properties of CeO<sub>2</sub>. As a result of that, these oxides are capable of “adsorbing” oxygen reversibly [25], a property that is used in catalytic converters of automobiles as a source of oxygen when the effluent from the engine has a reducing nature [26]. The high activity of the CuO–CeO<sub>2</sub> system is attributed to the strong interaction between Cu nanoparticles and the CeO<sub>2</sub> support. This interaction causes the reduction of the support and of the small CuO clusters to occur at low temperature [24,27]. In this way, adsorption of CO produces an easy reduction of the catalyst’s surface with the generation of CO<sub>2</sub> at low temperature. A mechanism that involves redox processes of the sites at the CuO–CeO<sub>2</sub> interface and also involves the presence of O<sub>2</sub><sup>–</sup> as an intermediary was proposed some years ago by Martínez-Arias et al. [28] for the oxidation of CO with O<sub>2</sub> over a CuO/CeO<sub>2</sub> catalyst. The mechanism involves reduction and adsorption of CO on the interface sites and reoxidation of the surface by O<sub>2</sub> from the gas phase in a Mars Van Krevelen type mechanism. Recently, the same author [29] showed that reduction of the surface of a CuO/CeO<sub>2</sub>

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catalyst starts at the interfacial CuO–CeO<sub>2</sub> positions, followed by reduction of CuO, and finally reduction of the rest of the CeO<sub>2</sub> that is not in contact with the copper oxide.

Although the binary CuO–CeO<sub>2</sub> catalysts show good performance in the PROX reaction, several studies have been made in parallel with the purpose of improving their efficiency and stability, incorporating other components, either as activity promoters or simply as supports.

In the case of the CuO–CeO<sub>2</sub> system supported on Al<sub>2</sub>O<sub>3</sub>, the studies have shown that the addition of CeO<sub>2</sub> increases considerably the activity of Cu supported on alumina [18–20]. The kind of species formed by cerium oxide supported on alumina has been studied, among others, by Martínez-Arias et al. [30]. They studied various ceria samples (loadings between 1% and 39%) on alumina (200 m<sup>2</sup>/g). The cerium species found on the alumina surface are mainly highly dispersed CeO<sub>2</sub> crystalline aggregates of a two-dimensional (2D) and three-dimensional (3D) type. The presence of different CeO<sub>2</sub> species on the alumina surface produces, as expected, differences in the Cu activity in CuO–CeO<sub>2</sub> catalysts supported on alumina, as shown in a previous report by Martínez-Arias et al. [31]. The results obtained show that the copper species in contact with the 3D CeO<sub>2</sub> species are reduced easily at temperatures below 100 °C, and they would be responsible for the high activity of the CuO–CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts.

Several years ago Fornasiero et al. [32] found that the mixed CeO<sub>2</sub>–ZrO<sub>2</sub> oxides with a Ce/Zr mole ratio equal to one had far better redox properties than those of the separate oxides. Thus, the incorporation of zirconia results in a highly efficient Ce<sup>4+</sup> ↔ Ce<sup>3+</sup> cycle at moderate temperatures. Considering that oxidation of CO on CuO–CeO<sub>2</sub> involves the reduction of both CuO and the support, it was believed that CuO/CeZrO<sub>2</sub> catalysts could be even more active than CuO/CeO<sub>2</sub> catalysts [28]. The results, however, showed that this hypothesis was not fulfilled, and that the best catalyst was the binary CuO/CeO<sub>2</sub> system both in the absence [28] and in the presence of H<sub>2</sub> [21,22].

It seems clear, then, that the presence of zirconia does not favor the activity of the CuO–CeO<sub>2</sub> catalysts. However, it must be kept in mind that in these studies the zirconia and ceria form a solid solution on which the CuO is supported. The situation may be different if the system is prepared so that the characteristics of the CuO–CeO<sub>2</sub> and CuO–ZrO<sub>2</sub> binary systems are potentiated, as it is well known that Cu supported on ZrO<sub>2</sub> is a very active catalyst for CO oxidation with O<sub>2</sub> [33–35].

Considering the above, the objective of this work was to study the effect of different supports on the activity of the CuO–CeO<sub>2</sub> system. As a first approximation, the study was carried out in the absence of H<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, and SiO<sub>2</sub> were considered as supports. To our best knowledge, the effect of SiO<sub>2</sub> on the activity of the CuO–CeO<sub>2</sub> system has not been studied previously, and it was included due to its well-known inert character. It is expected that the CuO and CeO<sub>2</sub> species formed on SiO<sub>2</sub> should be different from those formed on ZrO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, where it is known that there is an important interaction between the Cu species and the support. The loading, 2% Cu and 8% Ce, was chosen considering the work of Park et al. [17], who reported those concentrations as optimal for the CuO–CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> system, but obviously this is one of the variables that will be studied in later work on SiO<sub>2</sub> and ZrO<sub>2</sub> supports.

## 2. Experimental

The catalysts were prepared by coimpregnation of the support with a solution containing Cu and Ce nitrates, with a total loading of 2% Cu and 8% Ce. They were then dried at 105 °C overnight and calcined at 500 °C for 3 h in a muffle furnace. The supports used were ZrO<sub>2</sub>, obtained by calcination at 700 °C for 3 h of anhydrous

zirconium supplied by MEI; Al<sub>2</sub>O<sub>3</sub> was obtained by grinding agglomerated  $\gamma$ -alumina (BASF) and separating the fraction smaller than 100 mesh, and Aerosil 200 (Degussa) was used directly as a source of silicon oxide. Furthermore, a catalyst with 2% Cu supported on CeO<sub>2</sub> was prepared. Cerium oxide was obtained by calcination of cerium nitrate at 550 °C for 4 h, and it was then impregnated with a solution of copper nitrate and subjected to the same drying and calcination treatment described above.

The characterization of the supports and catalysts included N<sub>2</sub> sorptometry, XRD, Raman spectroscopy, and temperature programmed reduction with H<sub>2</sub> (TPR).

Determination of the BET specific area by N<sub>2</sub> sorptometry was made on Micromeritics ASAP 2010 equipment after degassing the sample at 200 °C. The crystal structure of the different catalysts and supports was determined on a Siemens D-5000 diffractometer using Cu K $\alpha$  radiation and a scan rate of 0.02°/min.

Raman spectroscopy was performed with a Renishaw Microscope System RM1000 using an Argon ion laser as an illumination source (514.5 nm) and CCD detector electrically cooled. The Raman equipment was coupled to a LECA microscope (50 $\times$  magnifications) and the collection optics was used in the backscattering configuration. The laser power was in the 1.0–3.0 mW to prevent heating of the sample.

Finally, the TPR analysis was made on conventional equipment with a TCD detector at a flow of 20 cm<sup>3</sup>/min of a 5% H<sub>2</sub>/Ar mixture and a heating ramp of 10 °C/min.

The kinetics tests were made in a piston flow tubular reactor, with a current of 2% CO and 3% O<sub>2</sub> at a total flow rate of 100 cm<sup>3</sup>/min. After loading the reactor with 0.2 g of catalyst, the sample was pretreated at 300 °C for 1 h in O<sub>2</sub>, and the reactor was cooled to room temperature. The reactants were then fed and the temperature was increased at a rate of 3 °C/min, taking samples every 20 °C to determine the concentration of CO, O<sub>2</sub>, and CO<sub>2</sub> on a PerkinElmer Autosystem chromatograph with a CTR column (Alltech) and a TCD detector.

## 3. Results and discussion

### 3.1. Characterization of the solids

#### 3.1.1. N<sub>2</sub> sorptometry

The results of the physical characterization of supports and catalysts by N<sub>2</sub> sorptometry are shown in Table 1. It is seen that the specific area does not vary significantly when impregnating the cerium and copper oxides on ZrO<sub>2</sub> and SiO<sub>2</sub>. When Al<sub>2</sub>O<sub>3</sub> was used as support a slight decrease was seen in the catalyst's area, in agreement with literature reports [36]. Among the three supports used, ZrO<sub>2</sub> is the one that has the smallest specific area, but as will be shown below, it is still capable of dispersing a substantial amount of copper on its surface due to a strong interaction between the Cu species and the support.

#### 3.1.2. XRD analysis

The results of the XRD analysis of the catalysts supported on Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, and SiO<sub>2</sub>, as well as those of the pure supports, are shown in Fig. 1(A–C), respectively. Fig. 1(D) shows the XRD spectra of the pure CeO<sub>2</sub> support and of the CuO/CeO<sub>2</sub> catalyst prepared on that support. All the figures include the principal diffraction lines of the cerium and copper oxides as reference.

In Fig. 1(A) it is seen that when Al<sub>2</sub>O<sub>3</sub> is used as support, none of the catalysts that contain Cu show the diffraction peaks of bulk CuO, indicating that in all the catalysts the Cu is highly dispersed on the support. This is not strange considering that the limit above which bulk CuO is formed is approximately 4% Cu for every 100 m<sup>2</sup>/g of Al<sub>2</sub>O<sub>3</sub> [37,38]. Therefore, since in our case the Cu

**Table 1**  
Physical characterization of the catalysts

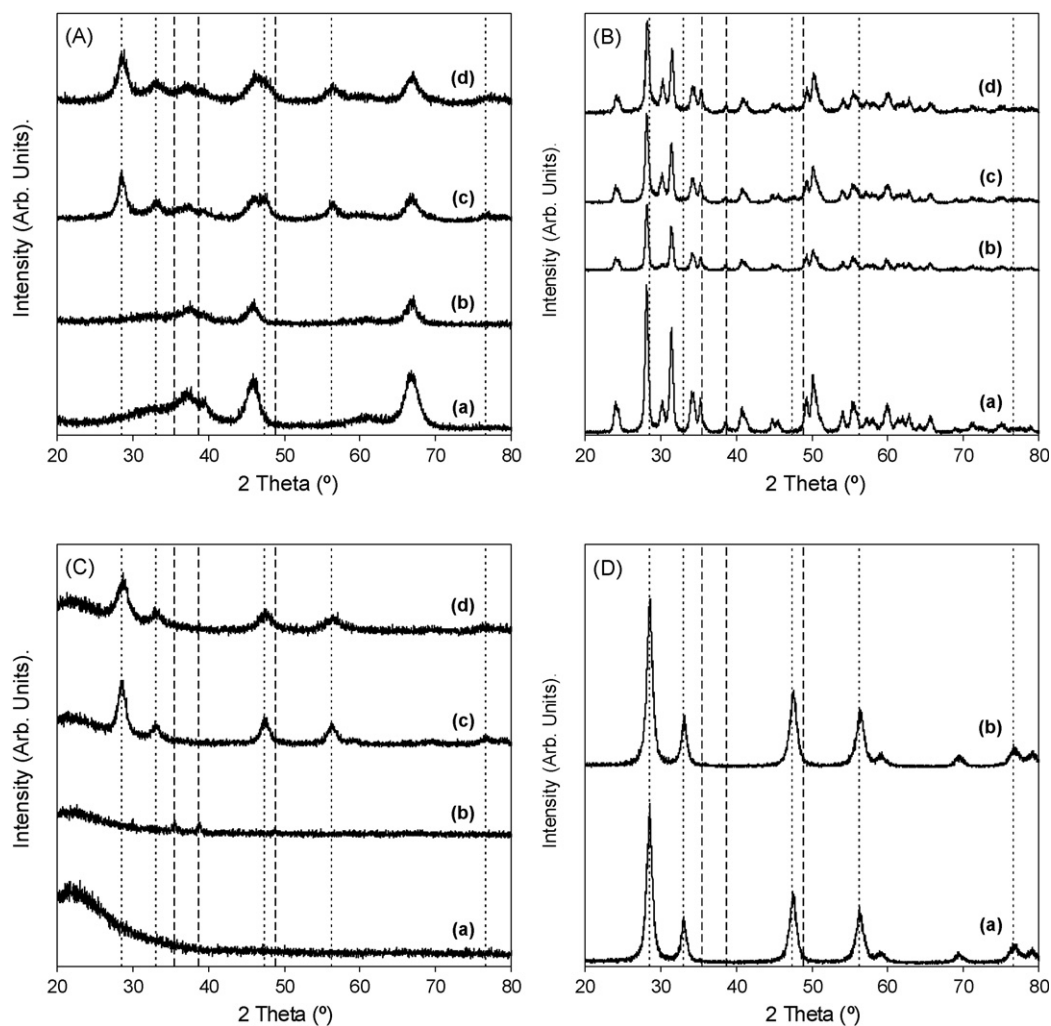
Sample	BET surface area (m <sup>2</sup> /g)	CeO <sub>2</sub> particle size (nm) <sup>a</sup>
Al <sub>2</sub> O <sub>3</sub> support		
Al <sub>2</sub> O <sub>3</sub>	208	
2%Cu/Al <sub>2</sub> O <sub>3</sub>	210	
8%Ce/Al <sub>2</sub> O <sub>3</sub>	181	8.7
2%Cu8%Ce/Al <sub>2</sub> O <sub>3</sub>	174	7.1
ZrO <sub>2</sub> support		
ZrO <sub>2</sub>	32	
2%Cu/ZrO <sub>2</sub>	33	
8%Ce/ZrO <sub>2</sub>	33	–
2%Cu8%Ce/ZrO <sub>2</sub>	32	–
SiO <sub>2</sub> support		
SiO <sub>2</sub>	195	
2%Cu/SiO <sub>2</sub>	196	
8%Ce/SiO <sub>2</sub>	198	9.0
2%Cu8%Ce/SiO <sub>2</sub>	182	7.6
CeO <sub>2</sub> support		
CeO <sub>2</sub>	87	
2%Cu/CeO <sub>2</sub>	79	10.2

<sup>a</sup> Estimated by XRD using the (1 1 1) face.

loading capacity was only 2% on an alumina of 200 m<sup>2</sup>/g, the dispersion capacity of alumina has not been surpassed, and the Cu should be expected to be highly dispersed, forming a structure of the Cu aluminate type [37].

In the case of the catalysts that contain cerium oxide, CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and CuO–CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, the characteristic peaks of crystalline CeO<sub>2</sub> are clearly seen, in agreement with literature reports [19]. The particle size of CeO<sub>2</sub> in these catalysts, estimated by XRD, is 8.7 and 7.1 nm, respectively, as shown in Table 1. These values agree quite well with those reported by Martínez-Arias et al. [31], who found CeO<sub>2</sub> particle between 8 and 10 nm for the same systems.

The XRD spectra of the catalysts supported on ZrO<sub>2</sub> are shown in Fig. 1(B). Analysis of the different catalysts shows that the peaks of the support dominate the XRD spectrum, making very difficult the direct observation of peaks corresponding to CuO and CeO<sub>2</sub> because they overlap those of the support. For that reason a detailed analysis of those spectra will not be made. However, analysis of the spectrum of the pure support shows the peaks corresponding to a mixture of monoclinic and tetragonal zirconia, whose proportions have already been calculated in a previous work, and correspond to 83% monoclinic and 17% tetragonal [39]. The particle size of CeO<sub>2</sub> is not reported in Table 1 because of the problems mentioned above.



**Fig. 1.** XRD patterns of various catalysts and supports. (A) Al<sub>2</sub>O<sub>3</sub> support: (curve a) pure Al<sub>2</sub>O<sub>3</sub>; (curve b) CuO/Al<sub>2</sub>O<sub>3</sub>; (curve c) CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>; (curve d) CuO–CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>. (B) ZrO<sub>2</sub> support: (curve a) pure ZrO<sub>2</sub>; (curve b) CuO/ZrO<sub>2</sub>; (curve c) CeO<sub>2</sub>/ZrO<sub>2</sub>; (curve d) CuO–CeO<sub>2</sub>/ZrO<sub>2</sub>. (C) SiO<sub>2</sub> support: (curve a) pure SiO<sub>2</sub>; (curve b) CuO/SiO<sub>2</sub>; (curve c) CeO<sub>2</sub>/SiO<sub>2</sub>; (curve d) CuO–CeO<sub>2</sub>/SiO<sub>2</sub>. (D) CeO<sub>2</sub> support: (curve a) pure CeO<sub>2</sub>; (curve b) CuO/CeO<sub>2</sub>. The characteristic peaks of CuO (---) and CeO<sub>2</sub> (· · ·) are included as reference.

The XRD spectra of the catalysts supported on SiO<sub>2</sub> are shown in Fig. 1(C). It is seen that the spectrum of the CuO/SiO<sub>2</sub> catalyst shows the peaks characteristic of bulk CuO at 35.5° and 38.7°. The formation of bulk CuO on silica, even at Cu loadings smaller than 2%, was reported previously [40], and it indicates the low interaction between the support and the Cu oxide.

The CeO<sub>2</sub>/SiO<sub>2</sub> catalyst shows the peaks attributed to CeO<sub>2</sub>, which are also seen in the CuO–CeO<sub>2</sub>/SiO<sub>2</sub> catalyst. However, as seen in Table 1, the size of the cerium oxide particles supported on SiO<sub>2</sub> decreases from 9.0 to 7.6 nm when both oxides are present on the surface of the silica. Although the size of the CeO<sub>2</sub> particles does not vary substantially when Cu and Ce are coimpregnated, the effect on the size of the CuO particles is more important. In fact, the peaks corresponding to CuO, which appear in the CuO/SiO<sub>2</sub> catalyst, are no longer seen in the CuO–CeO<sub>2</sub>/SiO<sub>2</sub> catalyst. This suggests that the simultaneous impregnation of Cu and Ce nitrates favors a high dispersion of CuO with a particle size not detectable by XRD. A similar effect has been reported by Xiaoyuan et al. [41] for CuO–CeO<sub>2</sub> catalysts supported on Al<sub>2</sub>O<sub>3</sub> using high copper loadings (10% Cu). Obviously, this effect is not seen with our catalysts supported on alumina, because due to the low copper loading used no bulk CuO is formed on alumina.

Finally, the XRD diagrams of the CeO<sub>2</sub> support and the 2% CuO/CeO<sub>2</sub> catalyst, which are presented in Fig. 1(D), shows the

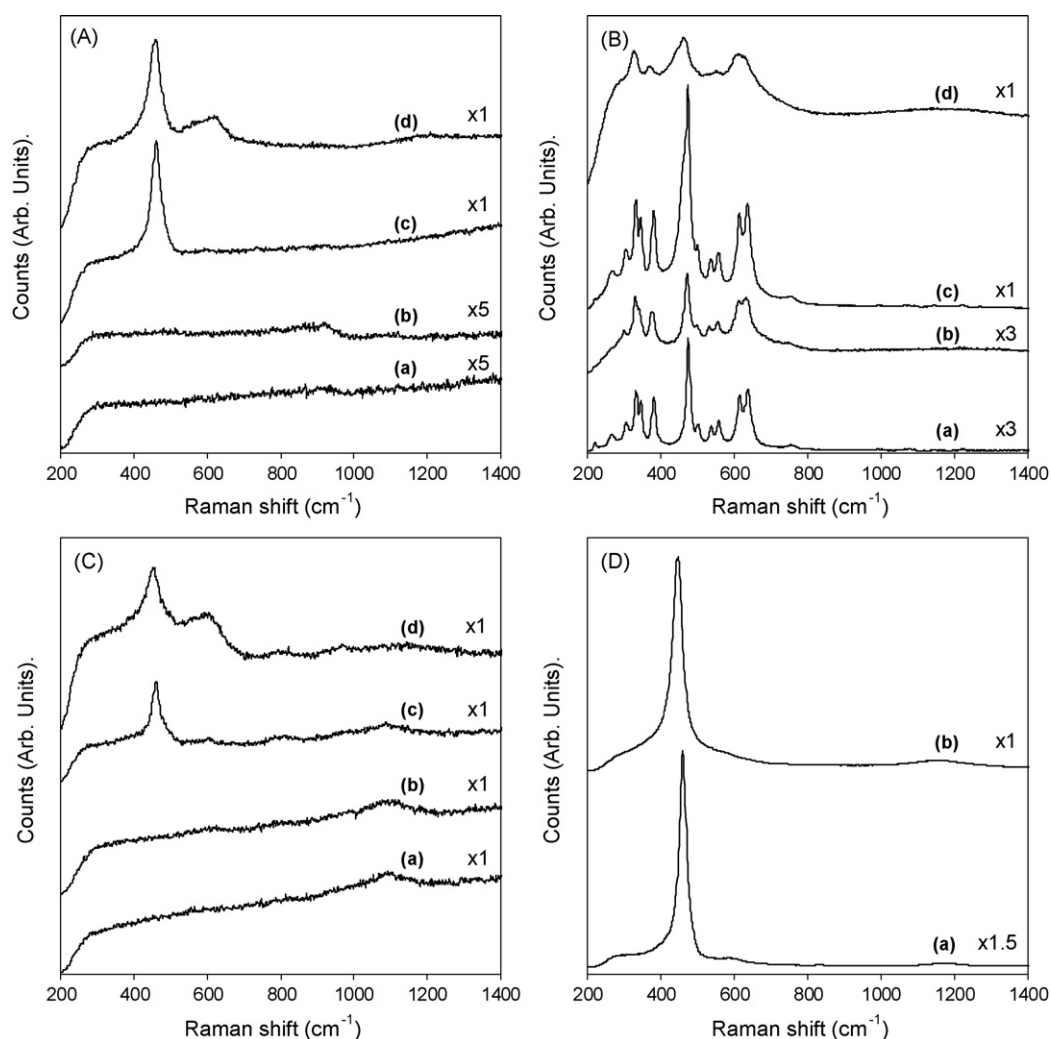
characteristic peaks of the fluorite type structure of CeO<sub>2</sub>. According to literature reports [15,36,42], at that copper loading crystalline CuO is not detected in the CuO/CeO<sub>2</sub> catalyst, indicating that this species is highly dispersed on the cerium oxide. According to Hu et al. [36], crystalline CuO is seen at loadings greater than 4.9% Cu on a cerium oxide of 58 m<sup>2</sup>/g, so it cannot be expected to see crystalline CuO in our catalyst, which has 2% Cu on a cerium oxide with an area greater than 80 m<sup>2</sup>/g.

### 3.1.3. Raman analysis

The Raman spectra of the catalysts supported on alumina, zirconia and silica are shown in Fig. 2(A–C), while the spectra of cerium oxide and of the copper catalyst supported on that oxide are shown in Fig. 2(D).

As seen in Fig. 2(A), in the case of the CuO/Al<sub>2</sub>O<sub>3</sub> catalyst there are no peaks around 290, 340 and 630 cm<sup>-1</sup> attributed to bulk CuO [43–45], indicating that CuO is highly dispersed over the support, in agreement with the XRD results.

The CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and CuO–CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts show clearly the CeO<sub>2</sub> peak at 460 cm<sup>-1</sup> corresponding to the triply degenerate F<sub>2g</sub> mode of fluorite CeO<sub>2</sub> [16,46]. In the CuO–CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst the peak corresponding to CeO<sub>2</sub> remains practically in the same place, but there is an additional wide peak at about 620 cm<sup>-1</sup>. The appearance of a peak around 600 cm<sup>-1</sup> has been reported by



**Fig. 2.** Raman spectra of various catalysts and supports. (A) Al<sub>2</sub>O<sub>3</sub> support: (curve a) pure Al<sub>2</sub>O<sub>3</sub>; (curve b) CuO/Al<sub>2</sub>O<sub>3</sub>; (curve c) CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>; (curve d) CuO–CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>. (B) ZrO<sub>2</sub> support: (curve a) pure ZrO<sub>2</sub>; (curve b) CuO/ZrO<sub>2</sub>; (curve c) CeO<sub>2</sub>/ZrO<sub>2</sub>; (curve d) CuO–CeO<sub>2</sub>/ZrO<sub>2</sub>. (C) SiO<sub>2</sub> support: (curve a) pure SiO<sub>2</sub>; (curve b) CuO/SiO<sub>2</sub>; (curve c) CeO<sub>2</sub>/SiO<sub>2</sub>; (curve d) CuO–CeO<sub>2</sub>/SiO<sub>2</sub>. (D) CeO<sub>2</sub> support: (curve a) pure CeO<sub>2</sub>; (curve b) CuO/CeO<sub>2</sub>.











