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CuO-CeO$_2$ catalytic systems destined for CO removal synthesized by means of the Pechini method: An evaluation of the structures obtained

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In this work, catalytic systems based on CuO-CeO$_2$ were synthesized by the Pechini method. These catalytic systems were prepared without the need to perform a step of impregnation of active species as is often seen in works of catalyst preparation. In the synthesis procedure, the CuO-CeO$_2$ catalytic systems were synthesized with 0.1 and 0.5 mol of CuO. The CuO-CeO$_2$ catalytic systems were characterized by X-ray diffraction (XRD) with the Rietveld refinement method, Energy Dispersive X-ray spectrometry (EDX), Scanning Electron Microscopy (SEM), textural analysis, thermogravimetry and agglomerates size distribution. According to the results, the CuO concentration value (0.1 or 0.5 mol) inserted into the CuO-CeO$_2$ catalytic system showed great influence on the structural characteristics observed in the X-ray diffraction results. However, the morphologic and textural features as well as the results of agglomerates size distribution did not show significant changes to the variation of CuO concentration inserted in the catalytic systems developed in this work by the Pechini method. On the other hand, it was observed that these catalytic systems presented a good porous structure, which is favorable for the catalytic application in PROX process. The next stage of this work is the catalytic test in the PROX reaction.

Key words: CuO-CeO$_2$ catalytic system, Pechini method, CO removal, PROX process.

INTRODUCTION

Cerium oxide (CeO$_2$) has earned intensive interest in the past decade because it plays a vital role in emerging technologies for environmental and energy-related application (Sun et al., 2004; Trovarelli, 1996; Carrettin et al., 2004; Park et al., 2000). Among a variety of oxides, ceium oxide is particularly of interest in a variety of catalytic processes. For instance, ceria has been used as catalyst or support in the selective oxidation, fine chemicals synthesis, methane steam reforming, phenol hydrogenation at atmospheric pressure and solid oxide fuel cell applications (Chojnscki et al., 1991; Yee et al., 1999; Putna et al., 1995, Craciun et al., 1998; Oh and Sinkevitch, 1993).

One of the important applications of ceria is its use in the area of environmental catalysis, particularly in the design of new generation of three-way catalysts for simultaneously controlling NO, CO and hydrocarbon emissions in oxygen-rich conditions. This is because ceria has large oxygen storage capacity and the ability of fastly transferring bulk oxygen to its surface (Crucq, 1991; Fornasiero et al., 1999). The former may uptake oxygen under fuel-lean conditions and the latter may release oxygen under reducing conditions, thus allowing a ceria-containing catalyst to efficiently work in a relatively wide window of oxygen partial pressure. In addition, ceria may also improve metal dispersion on it and promote surface and bulk oxygen reducibility of the support when it is used as a catalyst additive (Leitenburg et al., 1997; Kondarides et al., 1998).

In the last years, much research efforts have been focused on finding and developing a catalyst which is suitable to selectively oxidize CO (CO removal), also known as preferential oxidation of CO. Such a catalyst

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should be active for the oxidation of CO, and inactive for the undesired oxidation of H_2, in the temperature range of 80 to 250 °C. Supported noble metal catalysts especially Pt-group and Au catalysts, have been extensively studied (Avgouropoulos and Ioannides, 2007). However, the high cost of precious metals has encouraged researchers around the world to look for alternative catalysts. In particular, it has been found that the CuO–CeO$_2$ catalytic system is highly active and exceptionally selective for the preferential oxidation of CO (Haruta, 1997; Mariño et al., 2004; Marques et al., 2006; Kandoi et al., 2004; Martínez-Arias et al., 2006). A strong synergetic effect between copper and ceria has been reported to be responsible for the high activity of these catalysts compared to conventional Cu-based catalysts (Mariño et al., 2005).

In the literature, noble metal catalysts (Au, Pt and Ru) and oxide catalyst of CuO–CeO$_2$ have been developed for PROX process. Gold-based catalysts are active at low reaction temperature (~ 80°C) but their activities are seriously affected by CO_2 and excessive H_2O in hydrogen-rich gas (Avgouropoulos et al., 2002). Pt and Ru catalysts are active at medium reaction temperature (~ 140°C) but relatively low in selectivity of CO oxidation (<50%) (Manaslip and Gulari, 2002; Han et al., 2004). Comparably, CuO–CeO$_2$ catalysts have advantages of low cost and high selectivity of CO oxidation.

The chemical synthesis method based on polyesters obtained from citrates was developed by Pechini (Pechini, 1967) and is intensively used for the synthesis of several polycation metallic oxides (Lessing, 1989; Error and Anderson, 1986). This Pechini method is based on chelation or complexation of cations by hydroxycarboxylic acid such as citric acid. The source of cations can be diverse. The chelation process occurs during the mix of cations and citric acid in aqueous solution. This solution, with no particle in the suspension, is mixed with a glycol such as ethylene glycol and heated up to 90 to 100°C until complete water elimination. Polymerization occurs at 120 to140°C through the polyesterification reaction among citrate salt and ethylene glycol. Thus the formation of transparent solid polyester resin with no phase segregation is observed in this condition. The general idea of this method is to obtain a random distribution of cations at atomic level in a solid resin. After this stage the polyester is decomposed to eliminate the excess organic material and the cation is oxidized to form the desirable stoichiometric phase.

In this work, the CuO-CeO$_2$ catalytic system was synthesized by the Pechini method. The obtained catalytic systems were subject to various characterizations techniques to analyse structural characteristics for the knowledge of the same. After this research, these same synthesized catalytic systems in the work will be subject to tests, specifically in the preferential oxidation of CO reaction (PROX) in the bench scale.

MATERIALS AND METHODS

The CuO-CeO$_2$ catalytic systems were synthesized by the Pechini method using the following precursors: citric acid, cerium nitrate, copper nitrate, and ethylene glycol, all of them of high purity. Initially a solution using distilled water, nitrates (metal ions sources), citric acid and ethylene glycol, was prepared under constant agitation at a temperature of 70°C. After adding all the mentioned precursors, the obtained solution was heated at a temperature of polyesterification reaction (~ 120°C) to form a resin. The resin formed had undergone a pre-calcination stage (~ 400°C) for removing organic matter excess from the ethylene glycol, generating as product a carbonized material still containing traces of organic matter. This product was broken, sieved in a 325 mm mesh, and then subjected to a calcination stage at 700°C to eliminate the remaining organic matter, and also the formation of the desired phase (CuO-CeO$_2$) in the developed material structure. The final product obtained after the calcination stage was the desired catalytic system, which proceeded to the characterizations stage. Thus, the catalytic system based on CuO-CeO$_2$ was obtained without the necessity of performing an additional step of impregnation for incorporation of active species that in this case is copper oxide. The CuO-CeO$_2$ catalytic system was fully prepared in only step that is, the synthesized Pechini method was able to promote the preparation of this catalyst system without requiring additional steps.

In this work, two catalytic systems based on CuO-CeO$_2$ were synthesized; one containing 0.1 mol of CuO and another 0.5 mol of CuO. The samples of the CuO-CeO$_2$ catalytic system containing 0.1 mol of CuO was called P1, and the samples of the CuO-CeO$_2$ catalytic system containing 0.5 mol of CuO was called P5. The samples of the catalytic systems were submitted to the following characterization techniques: structural analysis by X-ray diffraction (XRD) using a Shimadzu XRD 6000 diffractometer (with CuKα radiation, λ = 0.15418 nm) combined with Rietveld refinement realized through the Maud Software; chemical analysis by Energy Dispersive X-ray spectrometry (EDX) using a Shimadzu EDX-GP spectrometer; morphological analysis by means of Scanning Electron Microscopy (SEM) in a ZEISS DSM 940 microscope; textural analysis by BET method using N$_2$ gas in Quantachrome Nova 3200 analyser; thermogravimetric analysis was performed on an analyzer TA instrument, model SDT 2960. This thermogravimetric analysis was performed at a temperature range of between 25 and 1000°C using a heating rate of 10°C min^{-1} and an inert atmosphere of N$_2$ and the agglomerates size distribution was determined using a CILAS 1064 LD particle size analyzer.

RESULTS AND DISCUSSION

Figure 1 shows the x-ray patterns of the data collected before (referencial or theoretical) and after (refined) Rietveld refinement referring to CuO-CeO$_2$ catalytic systems synthesized by the Pechini method defined as P1 and P5. According to the x-ray patterns referring to P1 sample, it was observed that it is possible to synthesize CuO-CeO$_2$ catalytic system with 0.1 mol of CuO and to obtain the formation of structure crystalline composed by CeO$_2$ as a single phase, that is, it is possible to obtain the desired structure (CuO-CeO$_2$) without the presence of segregated phases composed by CuO by means of Pechini method synthesis. The x-ray patterns referring to P5 sample shows that the concentration of 0.5 mol of CuO was sufficient to favor the formation of the
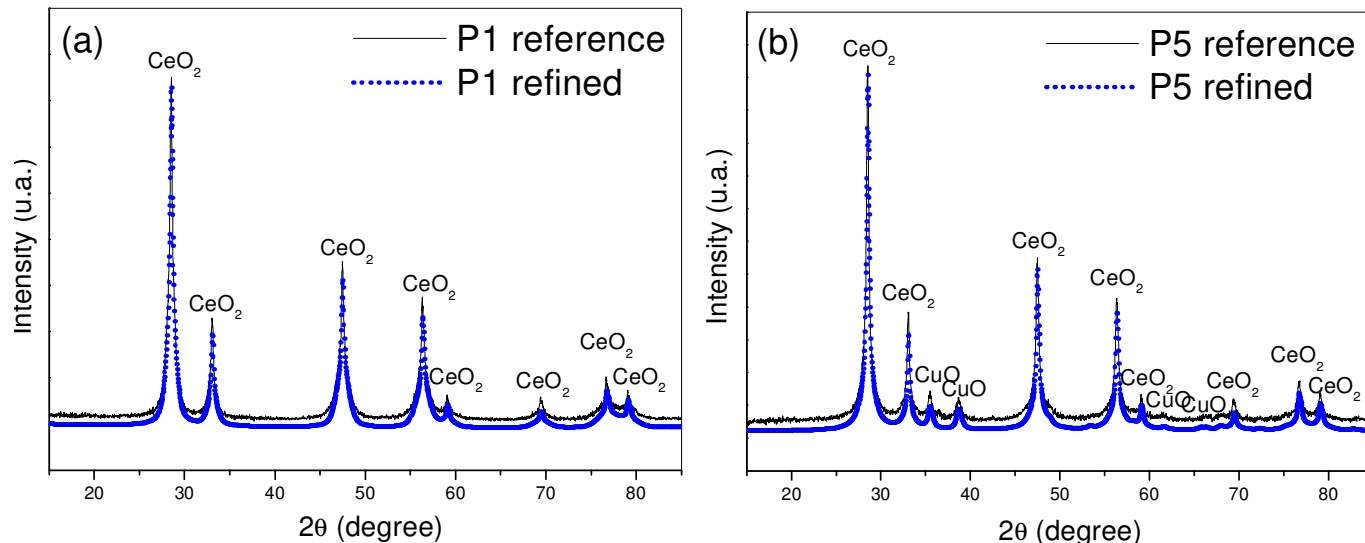
Figure 1. X-ray diffraction patterns before and after Rietveld refinement for the P1 and P5 catalytic systems synthesized by the Pechini method.

Table 1. Results of the quantification of the phases and others structural characteristics determined by the Rietveld method for the P1 and P5 catalytic systems synthesized by the Pechini method.

Sample	Phase	Crystalline system	Percentage mass (%)	Crystallite size (nm)
P1	CeO_2	Cubic	70.3	13.3
	CeO_2	Cubic	29.7	65.5
P5	CeO_2	Cubic	48.1	7.3
	CeO_2	Cubic	37.9	55.5
	CuO	Monoclinic	14.0	20.6

segregated phase composed by CuO over the structure of the CuO-CeO_2 catalytic system.

The structural characteristics determined by means of the Rietveld method for the CuO-CeO_2 catalytic systems synthesized by the Pechini method are shown in Table 1. According to the quantification of the phases formed in the analyzed structures, it can affirm that the predominant phase in both catalytic systems (P1 and P5) is the ceria phase (CeO_2). In the structure of the P1 sample containing 0.1 mol of CuO, it was not possible to detect the presence of the segregated phase of CuO. On the other hand, the P5 sample containing 0.5 mol of CuO presented the segregated phases composed by CuO over its structure with a massic percentage of 14%. This is an indication that the 0.1 mol of CuO concentration is within the solubility limit of CeO_2 atomic structure which in this case acts as a host matrix structure, that is, the structure of cerium oxide can incorporate 0.1 mol of CuO so that no remnant of copper oxide will be in an amount sufficient to form segregated phases over the structure of CeO_2. The same cannot be affirmed with respect to the

P5 sample containing 0.5 mol of CuO. Therefore, the concentration of CuO contained in the P5 sample certainly exceeds the solubility limit of the structure of cerium oxide. The proof is the presence of segregated phases composed by CuO in the synthesized structure.

It was also observed in Table 1 that both catalytic systems synthesized in this work presented in their structures the formation of two types of majority phases; both composed of CeO_2, but with different crystalline sizes. This difference in the crystalline sizes is a consequence of the calcinations step at 700 °C used in the synthesis procedure of the Pechini method. The calcination step promotes the coalescence of some crystals to form larger crystals, and thus, the final product can present phases composed by the same oxide but with different crystallite sizes. The phases formed in the structure of the P5 catalytic system belongs to different crystal systems (cubic and monoclinic) as can be seen in Table 1.

The chemical analysis results determined by EDX technique are presented in Table 2 and it shows that the

Table 2. Chemical composition determined by EDX technique for the P1 and P5 catalytic systems synthesized by the Pechini method.

Sample	CeO_2 (%)	CuO (%)	ZnO (%)	NiO (%)	LOI (%)
P1	90.97	7.89	0.18	0.12	0.84
P5	65.67	33.41	0.23	0.09	0.60
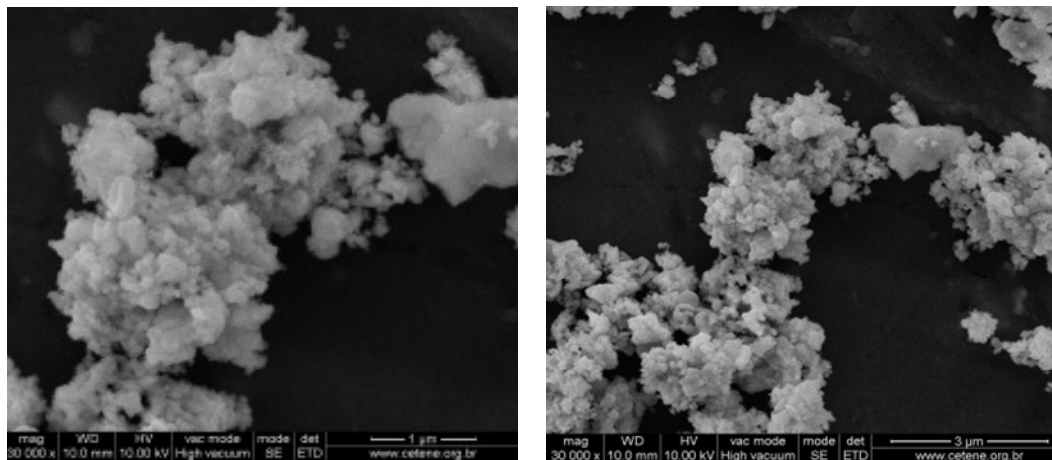
Figure 2. Micrographs obtained by SEM showing the morphology of the P1 and P5 catalytic systems synthesized by the Pechini method.

CuO-CeO_2 catalytic systems synthesized by the Pechini method are predominantly composed of CeO_2 and CuO. However, it was detected that the presence of the oxides, ZnO and NiO were probably incorporated into these catalytic systems by means of contaminants present in reagents, containers or ovens used in the synthesis procedure, or during the handling of these samples in the EDX analysis. The percentage of Loss on Ignition (LOI) was determined at the 1000°C.

Figure 2 illustrates the results of morphological evaluation performed by Scanning Electron Microscopy (SEM) in the CuO-CeO_2 catalytic systems synthesized by the Pechini method. The micrographs in Figure 2 show their respective images with a magnification of 30.000X.

According to the micrographs shown in Figure 2, the CuO-CeO_2 catalytic systems synthesized by the Pechini method presented a strong tendency to the state of particles agglomeration, forming noticeably porous structures. This morphology aspect is very appropriate from the point of view that potential catalytic properties are expected of these materials. It is worth pointing out that these catalytic systems present a relatively homogeneous size distribution of agglomerates. There appeared to be no significant differences between the morphological characteristics presented by the P1 and P5 catalytic systems therefore, it can be rationalized that the incorporation process of CuO in different concentrations (0.1 and 0.5 mol) did not alter the morphological characteristics of these materials. Similar

morphological characteristics were found in several other studies related to the preparation of cerium dioxide for application in catalytic reactions by different synthesis methods (Triki et al., 2009; Polato et al., 2005; Sun et al., 2007; Neiva et al., 2010).

Figure 3 shows N_2 adsorption-desorption isotherms referring to the textural analysis of CuO-CeO_2 catalytic systems synthesized by the Pechini method. According to the IUPAC classification (Sing et al., 1985), these isotherms can be considered as type III, characterizing porous materials with a predominantly macroporous nature. The hysteresis loop presented on these isotherms is of type H3, especially between P/P0 = 0.45 and 0.95 which reveals the presence of pores generally formed by the association of non-rigid agglomerates of particles (Figueiredo and Ribeiro, 1987).

Table 3 shows the values of the textural characteristics such as surface area (S_{BET}) determined by BET method, and values of pore volume (V_P) and medium pore diameter (D_P) determined by BJH method, all referring to CuO-CeO_2 catalytic systems called P1 and P5 synthesized by the Pechini method.

According to the values presented in Table 3, the medium pore diameter (D_P) of the CuO-CeO_2 catalytic systems synthesized in this work are of macroporous dimensions (D_P > 50 nm), which confirm the porosity type revealed in the isotherms presented in Figure 3.

In Table 3, it was also observed that the values of surface area, pore volume, and medium pore diameter
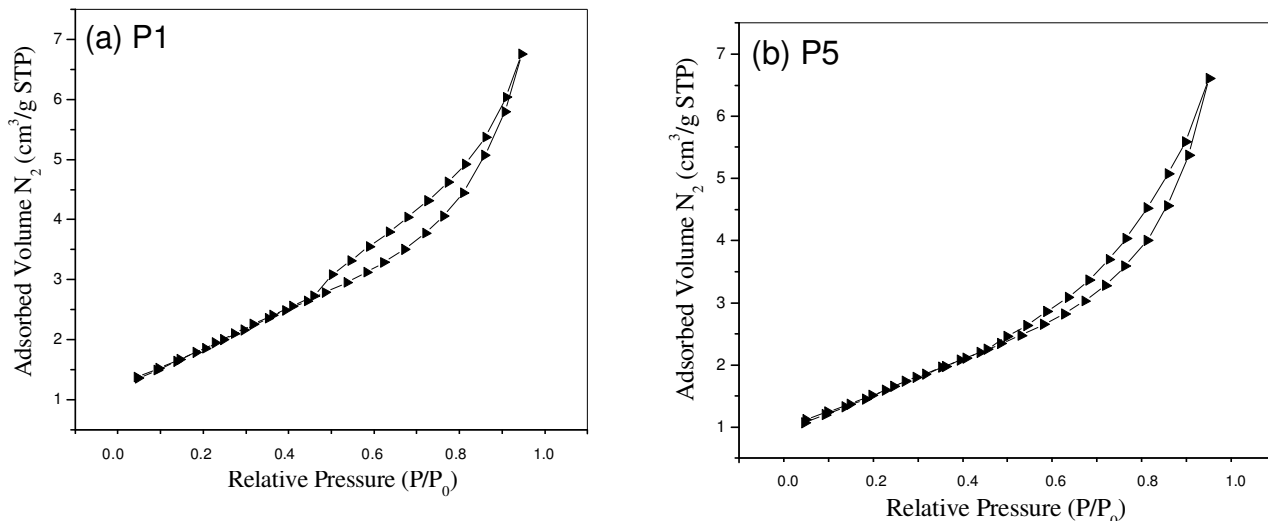
Figure 3. N_2 adsorption-desorption isotherms related to the P1 and P5 catalytic systems synthesized by the Pechini method.

Table 3. Surface area, pore volume and medium pore diameter determined for the P1 and P5 catalytic systems synthesized by the Pechini method.

Sample	S_{BET} (m^2/g)	V_P (nm)	D_P (nm)
P1	16	0.02204	387
P5	14	0.02251	383
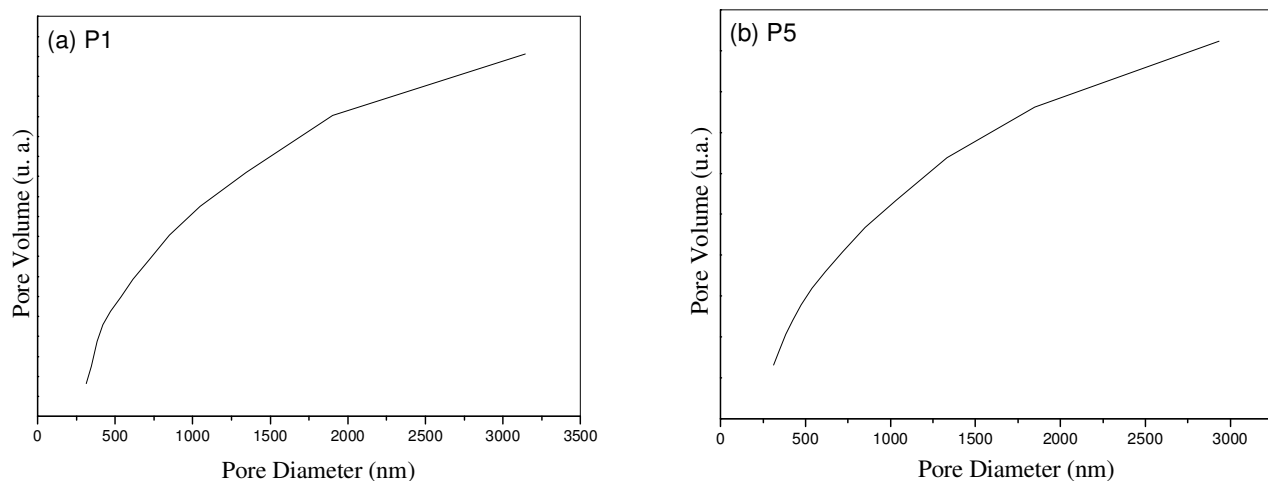
Figure 4. Graphs of pore diameter distribution of the P1 and P5 catalytic systems synthesized by the Pechini method.

did not present significant variations for the CuO concentrations incorporated in the synthesis of the CuO-CeO$_2$ catalytic systems (P1 and P5) by the Pechini method. This finding is viewed positively, since the CuO substance was inserted into the material structure, probably causing the formation of catalytic active sites without generating great changes in the textural characteristics of the structures.

Figure 4 presents graphs of pore size distribution referring to the CuO-CeO$_2$ catalytic systems called P1 and P5 synthesized by the Pechini method. The graphs of pore size distribution of the P1 and P5 catalytic systems synthesized by the Pechini method show that these materials present fully macroporous structures, as had been revealed by the isotherms shown in Figure 3 and the data shown in Table 3. Other researches
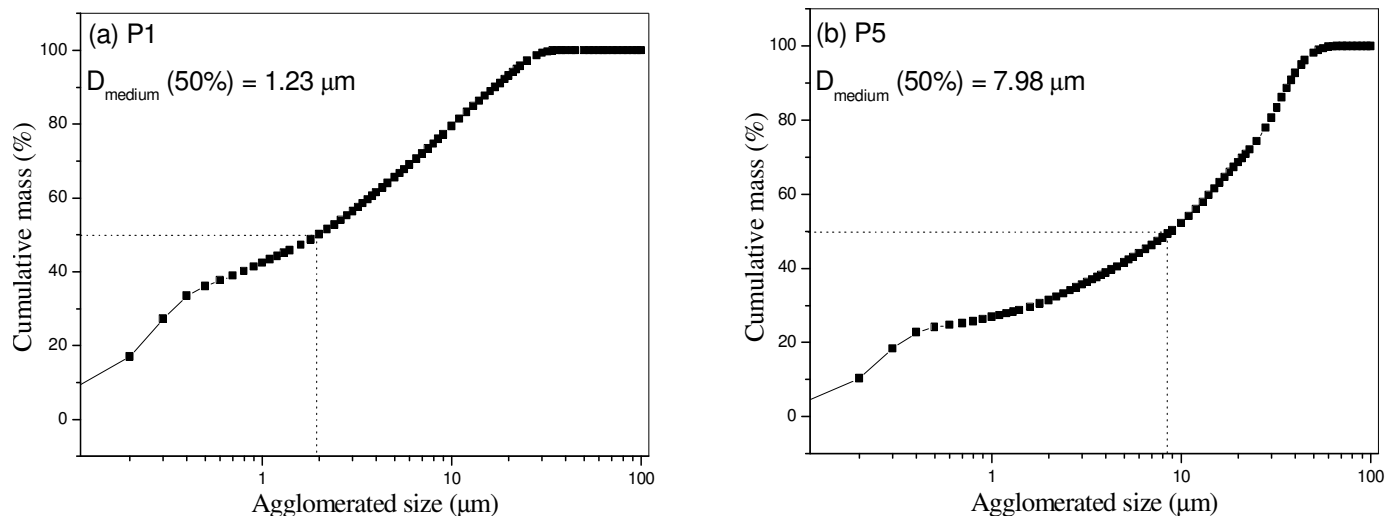
Figure 5. Agglomerates size distribution of the P1 and P5 catalytic systems synthesized by the Pechini method.

referring to CuO-CeO_2 catalytic system destined for preferential oxidation of CO has also been shown textural characteristics very similar to the observed for the CuO-CeO_2 catalytic systems obtained in this work (Qiang et al., 2007; Moretti et al., 2008).

According to the thermogravimetric analysis performed on samples of the catalytic system synthesized in this work using a temperature range of between 25 and 1000°C, the samples showed no weight loss throughout the temperature range studied. The calcination step at 700°C experienced by these samples during their synthesis was certainly sufficient to eliminate any concentration of organic matter and humidity, therefore, these samples remained inert resulting in mass loss during the thermogravimetric analysis.

Figure 5 shows the curves of agglomerates size distribution for the P1 and P5 catalytic systems. According to Figure 5, it is possible to observe that the curves of agglomerate size distribution present similar profiles between the systems under study. However, the P1 catalytic system presented a lower medium diameter ($D_{50\%}$) of agglomerates. Thus, it is possible to affirm that the particles' agglomeration capacity is directly related to the CuO concentration value inserted in the structure of these materials, that is, the particles agglomeration capacity is directly related to the CuO concentration value inserted in the structure of cerium oxide.

The study of the granulometric behavior of compound materials by single or mixed oxides can lead to a determination of suitable size of the grain for use as a control parameter for a specific application of the material, according to the elements or substances that constitute the material as well as with the conditions for obtaining them. A detailed analysis of this behavior can guarantee obtaining a catalytic system based on CuO-CeO_2 with more uniform and standardized structure.

Conclusions

According to the results we can affirm that it is possible to synthesize catalytic systems based on CuO-CeO_2 by means of the Pechini method, without the need for a step of impregnation of the active species catalysis as is often seen in researches on the preparation of catalysts. Also it can be affirmed that the catalytic system based on CuO-CeO_2 can incorporate 0.1 mol of CuO without forming segregated phase composed by CuO over the structure of the material when synthesized by the Pechini method. On the otherhand, the phases of quantification realized by the Rietveld method showed that the CuO-CeO_2 catalytic system containing 0.5 mol of CuO allowed the formation of a structure with mass percentage of 14% of the segregated phase composed of CuO. The CuO concentration value incorporated in the CuO-CeO_2 catalytic system synthesized by the Pechini method did not lead to significant alterations in the morphological and textural characteristics of these materials. On the other hand, it is possible to affirm that the particle agglomeration capacity of these catalytic systems is directly related to the CuO concentration value inserted in their structures.

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