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Effect of lanthanum on the properties of copper, cerium and zirconium catalysts for preferential oxidation of carbon monoxide

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ABSTRACT

Catalysts based on copper and cerium oxides are active and selective in preferential oxidation of carbon monoxide (CO-PROX) and then considered as promising for obtaining hydrogen with acceptable purity for proton exchange membrane fuel cell. However, the low specific surface area of cerium oxide leads to the production of large copper particles, which do not contribute to the catalyst activity. Aiming to find more efficient catalysts for this reaction, the effect of lanthanum on the properties of catalysts based on copper, cerium and zirconium was studied in this work. The samples ($CuO–Ce_{1−x}La_xO_{2−x/2}$ and $CuO–Ce_{0.5−x/2}Zr_{0.5−x/2}La_xO_{2−x/2}$; $x = 0.0$; 0.05; 0.10) were prepared by precipitation in alkaline medium and heated under air flow at $450\,°C$. They were characterized by ICP-OES, Fourier transform infrared spectroscopy, X-ray diffraction, Raman spectroscopy, specific surface area and porosity measurements, temperature programmed reduction, oxygen storage capacity measurements and isotopic exchange with oxygen-18. The catalysts were evaluated in CO-PROX from 150 to $300\,°C$. The zirconium-containing samples presented tetragonal structure while the zirconium-free ones showed face-centered cubic structure. Lanthanum and copper were incorporated into ceria lattice, while zirconia and ceria formed solid solutions. Zirconium increases the specific surface area by decreasing the particle crystal size and also created mesoporosity. Lanthanum decreased the interaction between copper and ceria while zirconium did the opposite. On the other hand, lanthanum increased the oxygen storage capacity and oxygen mobility whereas zirconium decreased it. Lanthanum did not improve the activity and selectivity of the catalysts in CO-PROX. Moreover, zirconium increased the activity, by increasing the interaction between cerium and copper and then increasing the interface where the reaction occurs. All catalysts were resistant against deactivation by water and the activity and selectivity could be recovered after poisoning by carbon dioxide.

1. Introduction

Over the years, the increasingly search for more efficient and cleaner routes for energy production as well as the concerning for protecting the environment have led to the development of new technologies, such as fuel cells. These devices have been pointed out as the most promising alternatives for the production of electricity in the future [1], especially when fed with hydrogen. Among the several available kinds, the proton exchange membrane fuel cell (PEMFC) is the most advanced one, being able to operate in both mobile and stationary applications [2].

In spite of the high stage of development, there are still some drawbacks to be overcome before the PEMFC can be widely used in commercial applications. One of them is related to the need of using CO-free hydrogen due to the susceptibility of the platinum electrocatalysts to be poisoned by carbon monoxide. Since nowadays most hydrogen is produced by steam reforming of naphtha or natural gas, the purification of the hydrogen-rich stream obtained is required, so that it becomes free or up to about 10 ppm of carbon monoxide [3]. In general, these streams contain around 0.5–2.0% of carbon monoxide [4,5], even after the purification steps by water gas shift reaction over iron based-catalysts at high temperatures [6,7] and then over copper and aluminum-based solids at low temperatures [8,9].

A promising route to purify the hydrogen-rich streams for fuel cells is through the preferential oxidation of carbon monoxide

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(CO-PROX). This process consists in the catalytic oxidation of carbon monoxide by molecular oxygen in the presence of high amounts of hydrogen. In this case, catalysts very selective to carbon monoxide oxidation should be used, since hydrogen can also be oxidized and other reactions can also occur [3]. Several catalysts fit this requirement such as those based on noble metals, including platinum, ruthenium and gold, which exhibit high catalytic activities. Platinum-based catalysts have been extensively studied for the oxidation of carbon monoxide, exhibiting high activity and selectivity, regardless the formulation. Therefore, alumina-supported platinum ($1\% Pt/Al_2O_3$) [10,11], ceria-supported platinum ($1\% Pt/CeO_2$), ceria and zirconia-supported platinum ($1\% Pt/Ce_{0.68}Zr_{0.32}O_2$) [12], zeolites-supported platinum (6.3% Pt/FAU) [13] and carbon nanotubes-supported platinum (2% Pt-3% Ni/CNT) [14] have been evaluated and have shown high activities and selectivities. Among these catalysts, alumina-supported platinum was identified as the most promising one, a fact that was assigned to its high metallic dispersion, related to the high specific surface area of the support [10,11]. However, they can produce methane at temperatures above 200 °C, consuming hydrogen and decreasing the process efficiency. Ruthenium-based catalysts have also shown high activities in CO-PROX although high methane production was often noted, increasing with the ruthenium concentration and the reaction temperature [15]. Gold-based catalysts have also been pointed out as good candidates for CO-PROX [16–18], for which the activity has been increased by the use of reducible supports such as iron oxide ($2.9\% Au/Fe_2O_3$) [10], titanium oxide (Au/TiO_2) [19], cerium oxide ($98\% Au/CeO_2$) [16], cerium and cobalt oxide ($1.4\% Au/Co_3O_4–CeO_2$) [20] and cerium and iron oxide ($3.4\% Au/CeO_2–Fe_2O_3\%$) [21]. The high activity of these catalysts can be associated with the stabilization of the ionic species (Au^+ and Au^{3+}) on the surface and to the presence of oxygen vacancies [20,22] as well as to the dispersion of gold nanosized particles [23].

In spite of the high performance of noble metals in CO-PROX reaction, their use is limited due to the low availability and high cost. Currently, ceria-supported copper has been pointed out as a less expensive alternative to noble metals [24]. Copper-based catalysts such as $5\% CuO–CeO_2$ [25] $CuO/Ce_{0.8}Ti_{0.2}O_2$ (8% Cu) [26], $CuO–Ce_{0.8}Zr_{0.2}O_2$ (7% Cu) [27], for instance, have been proved to be very active in CO-PROX-CO and selective to carbon dioxide. It was observed that the Ce(III)/Ce(IV) redox cycle favored the mobility of oxygen [28] and increased the activity. As a result, this catalyst can reversibly store oxygen and release it during reaction, favoring oxidation. However, a common problem of copper and cerium oxide-based catalysts is the production of large copper oxide particles, which do not contribute to the activity in CO-PROX [25,29]. Alternative synthesis routes can be used to obtain ceria with high specific surface area, allowing more dispersed copper particles [30]. Moreover, it was observed that the addition of rare-earth elements or zirconium to ceria can increase their specific surface areas [31,27], which can be used to increase the dispersion of copper and then to produce more active catalysts. It has also been shown that the addition of rare-earth elements to cerium or cerium–zirconium oxides may increase the oxygen storage capacity of these materials [32,33]. Furthermore, the addition of zirconium to cerium oxide increases the thermal resistance and the reducibility of the solid as well as the oxygen mobility [34]. It is expected that the addition of zirconium to copper and cerium oxides will improve its redox properties decreasing the reduction temperature and increasing the concentration of Ce^{3+} ions leading to an increased oxygen mobility in the lattice [29]. Therefore, more efficient alternative catalysts can be obtained by combining these properties. With this goal in mind, the effect of lanthanum on the properties of cerium and copper oxide ($CuO–CeO_2$) and of copper, cerium and zirconium ($CuO–Ce_{0.5}Zr_{0.5}O_2$) catalyst was studied in this work.

2. Experimental

2.1. Catalysts preparation

Samples were prepared by simultaneous precipitation of metal ions in basic medium. A solution containing copper nitrate, cerium nitrate, zirconium oxychloride and lanthanum nitrate was added to a potassium hydroxide solution at 70 °C under vigorous stirring. During precipitation, the pH was maintained at 10 by the addition of a potassium hydroxide solution ($2 \, mol \, L^{-1}$). After precipitation, the system was kept under stirring upon heating at 70 °C, for 2 h and then centrifuged, the solid obtained being washed with deionized water. After drying at 120 °C for 17 h, the solid was calcined at 450 °C, for 4 h, under air flow ($100 \, mL \, min^{-1}$).

2.2. Catalysts characterization

The catalysts were characterized by elemental chemical analysis, Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), Raman spectroscopy, specific surface area (Sg) and porosity measurements, temperature programmed reduction (TPR), oxygen storage capacity measurements and $^{18}O/^{16}O$ isotopic exchange technique.

The chemical composition of the samples was determined by optical emission spectrometry with inductively coupled plasma (ICP-OES) using a Perkin Elmer model Optima 2000 DV instrument. The experiments of Fourier transform infrared spectroscopy were obtained on an ABB-Bomem model MB 100 instrument. The samples were dispersed in potassium bromide and the spectra were collected using a resolution of $4 \, cm^{-1}$ with an accumulation of 32 scans.

The X-ray diffractograms were obtained on a Shimadzu model XRD 6000 apparatus using a CuK_α radiation generated at 40 kV and 30 mA with a nickel filter. The data were collected in a range of 5°–90° (2θ) with speed of 2° min^{-1}. The average crystal size was determined using the Scherrer Equation. The Raman spectra were obtained on a Jasco model NRS-5100 spectrometer, using a green laser of 532.13 nm, 6.1 mW and a resolution of $3.5 \, cm^{-1}$.

The specific surface area and porosity of the catalysts were measured by nitrogen adsorption/desorption at −196.15 °C by BET (Brunauer–Emmett–Teller) and BJH (Barrett–Joyner–Halenda) methods, respectively, using a Micromeritics ASAP 2020 instrument. Before analysis, the samples (0.2 g) were heated up to 350 °C under vacuum (150 μmHg) to remove water. The experiments of temperature-programmed reduction were performed in a Micromeritics model 2705 Pulse ChemiSorb apparatus. During analysis, the samples (0.03 g) were heated from 25 to 850 °C under a flow ($30 \, mL \, min^{-1}$) of a 5% H_2/N_2 mixture.

The oxygen storage capacity (OSC) measurements were carried out in an atmospheric glass fixed bed reactor placed in an electrical oven connected to a Porapak column and a TCD. The sample (0.006–0.008 g) was placed into the reactor and heated up to 400 °C under helium flow ($30 \, mL \, min^{-1}$) at atmospheric pressure. At this temperature, ten pulses (loop volume: 0.265 mL) of pure oxygen were introduced to oxidize completely the sample and a helium flow was passed through the sample for 10 min to purge it. Then, pure carbon monoxide pulses were injected up to a maximum reduction of the sample before a new purging step of 10 min with helium. The oxygen storage capacity (OSC) was calculated from the carbon dioxide production after the first pulse of CO: it represents the amount of oxygen atoms rapidly available in the material. Then, the oxygen storage complete capacity (OSCC) value was evaluated from the total amount of carbon monoxide consumed at the end of the carbon monoxide pulse series. The OSCC value corresponds to the total amount of reactive oxygen in the material.