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The influence of promoters (Zr, La, Tb, Pr) on the catalytic performance of $CuO-CeO_2$ systems for the preferential oxidation of CO in the presence of CO_2 and H_2O

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ABSTRACT

CuO supported on CeO_2 and $Ce_{0.9}X_{0.1}O_2$, where X is Zr, La, Tb or Pr, were synthesized using nitrate precursors, giving rise ceria based materials with a small particle size which interact with CuO species generating a high amount of interfacial sites. The incorporation of cations to the ceria framework modifies the CeO_2 lattice parameter, improving the redox behavior of the catalytic system. The catalysts were characterized by X-ray fluorescence spectrometry (XRFS), X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), Raman spectroscopy, thermoprogrammed reduction with H_2 (H_2-TPR) and X-ray photoelectron spectroscopy (XPS). The catalysts were tested in the preferential oxidation of CO under a H_2-rich stream (CO-PROX), reaching conversion values higher than 95% between 115 and 140 °C and being the catalyst with 6 wt.% of Cu supported on $Ce_{0.9}Zr_{0.1}O_2$ (sample 6CUZRCE) the most active catalyst. The influence of the presence of CO_2 and H_2O was also studied simulating a PROX unit, taking place a decrease of the catalytic activity due to the inhibitor effect both CO_2 and H_2O.

1. Introduction

In the last decades, new technologies have been developed for cleaner and more efficient energy production, and fuel cells have been pointed out as a promising alternative for this purpose. Among the several fuel cells available, the low-temperature proton exchange membrane fuel cell (PEMFC) has been largely studied in both mobile and stationary applications due to its high energy conversion at low temperature of operation (80 °C) [1]. The H_2 used in the PEMFC is usually obtained by steam reforming, partial oxidation, or auto-thermal reforming of liquid hydrocarbons or natural gas in combination with the water gas shift (WGS) reaction. However, the H_2-rich stream coming from the WGS reaction exhibits CO concentration of about 1–2 vol.%. These values cannot be tolerated by the PEMFC because the catalytic anode is extremely sensitive to CO poisoning at concentrations higher than 10 ppm.

Several methods have been proposed to diminish the CO content of the H_2-rich stream. The main methods to remove the CO are as follows: (i) purification with a H_2 selective membrane, (ii) CO methanation, (iii) pressure swing adsorption, and (iv) preferential oxidation of CO (CO-PROX). Among them, CO-PROX reaction has been considered as the straightforward and economical technique to minimize the CO content [2,3].

The CO-PROX catalysts must show high activity at the operating temperature of the fuel cells (80–120 °C) with a good resistance to deactivation by H_2O and CO_2. Moreover CO-PROX catalysts need to be also highly selective towards the oxidation of CO, minimizing the consumption of H_2 by unwanted oxidation to water and avoiding the loss of energy [4].

Traditionally, noble-metal based catalysts with Pd [5], Rh [6,7], Ru [8,9] and mainly Au [10,11] and Pt [12–14] have shown to be active phases in the CO-PROX reaction. In spite of the high conversion values, the high cost and the availability of the noble metals limit its high scale application. This fact has led to the development of cheaper and more available active phases which show high activity and much higher selectivity to CO. The use of non-noble metal based catalysts, mainly copper catalysts, has received special attention due to the high selectivity in the CO-PROX reaction [15]. The use of ceria to form a $CuO-CeO_2$ system has been highly tested in the literature [16–23]. The establishment of intimate contact between

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CuO and CeO_2 generates a synergic effect that increases the catalytic activity, in which Cu^+ species are stabilized by interaction between cooper oxide clusters and cerium oxide providing surface sites for easy CO adsorption [24].

Ceria is a key component in the catalytic system (CuO-CeO_2) due to the high ability to store and release oxygen [25]. Ceria exhibits two kinds of oxygen species available for its oxygen storage capacity (OSC), one being the surface oxygen and another the bulk oxygen. Besides limited bulk reducibility, pure ceria is associated with some other drawbacks like thermal sintering and deactivation of the Ce^{3+}/Ce^{4+} redox couple at high temperatures which result in the decline of OSC and catalytic activity. The doping of CeO_2 with isovalent/aliovalent cations can enhance the OSC, especially to improve the bulk reducibility at lower temperatures and to stabilize the structure against sintering [26].

The addition of isovalent cations as zirconium (Zr^{4+}) into the ceria framework increases the OSC by the formation of extrinsic oxygen vacancies that enhances the oxygen mobility by facilitating the Ce^{3+}/Ce^{4+} redox process, although the bulk oxygen mobility remains much less than the oxygen mobility at the surface [27]. The doping with aliovalent non-reducible cations such as lanthanum (La^{3+}) into the ceria framework enhances the OSC through the intrinsic oxygen vacancies [28]. The doping with variable valence cations into the ceria as terbium (Tb) and praseodymium (Pr) where coexist M^{3+} and M^{4+} oxidation states, (adopting M^{3+} oxidation state more easily than bulk ceria) [29], induces the formation of ordered intrinsic and extrinsic oxygen vacancies thereby enhance the OSC [30,31]. Despite of the doping is a key factor in the OSC, other factors can also influence the reducibility of ceria such as surface area, nature and distribution of dopant, oxygen vacancies and bulk oxygen mobility [32].

In the present research, a set of ceria based materials have been synthesized. These materials have been doped with isovalent cations such as zirconium, aliovalent non-reducible cations as lanthanum or variable valence cations as terbium or praseodymium which should provide diverse catalytic behavior to the ceria. These materials have been used as support of copper oxide to test the catalytic performance of this catalytic system in the CO-PROX reaction between 65 and 190 °C. Moreover the influence of the CO_2 and H_2O in the feed, simulating a PROX unit fed with a H_2-rich H_2O- and CO_2-containing gas flow coming from a water-gas-shift reactor, was also evaluated.

2. Experimental

2.1. Catalyst preparation

CeO_2 and $Ce_{0.9}X_{0.1}O_2$ mixed oxides, where (X = Pr, Zr, La or Tb) were prepared by proper mixture of $Ce(NO_3)_3{\cdot}6H_2O$ (Aldrich 99.99%) and $Pr(NO_3)_3{\cdot}6H_2O$ (Aldrich 99.9%), $ZrO(NO_3)_2{\cdot}xH_2O$ (Aldrich), $La(NO_3)_3{\cdot}6H_2O$ (Aldrich 99.99%) or $Tb(NO_3)_3{\cdot}5H_2O$ (Aldrich 99.9%), respectively, to have a Ce:X molar ratio of 9:1. The mixture was calcined in a muffle furnace (in static air) from 25 to 500 °C at 10 °C min^{-1}, maintaining the sample at 500 °C for 2 h. Note that the stoichiometric coefficient of oxygen in $Ce_{0.9}X_{0.1}O_2$ could be lower than 2, mainly for mixed oxides containing +3 cations, but the coefficient 2 has been kept in the formula for the sake of simplicity. In order to evaluate the total calcination of the precursor, CNH analysis were carried out, obtaining in all cases a nitrogen content lower than 0.5 wt.%.

Copper containing catalysts were prepared by incipient wetness impregnation of the supports with a solution of copper(II) acetate (6 wt.% Cu). After impregnation, the solids were dried overnight at 60 °C and calcined during 4 h at 400 °C. The catalysts were denoted 6CUXCE, where X is the doping agent added to the ceria.

2.2. Characterization methods

Elemental bulk composition of the catalysts in terms of Cu loading was determined by X-ray fluorescence spectrometry (XRFS) using a Horiba XGT-500 spectrometer with a probe diameter of 1.2 mm. The X-ray tube was set at 50 kV with an acquisition time of 500 s and a current intensity between 0.26 and 0.32 mA.

Powder XRD patterns for the samples were collected on a X'Pert Pro MPD automated diffractometer (PANalytical B.V.) equipped with a Ge(1 1 1) primary monochromator (strictly monochromatic $CuK\alpha_1$ radiation) and an X'Celerator detector with a step size of 0.017°. The powder patterns were recorded between 10° and 70° in 2θ with a total measuring time of 30 min. The particle size of CeO_2 and $Ce_{0.9}X_{0.1}O_2$ mixed oxides and the lattice strain were estimated by Williamson-Hall method with a fitting of the diffraction profile. The cell parameters were obtained from Rietveld method by using the XPért HighScore Plus software.

Elemental chemical analysis was performed for all calcined precursors with a LECO CHN 932 analyzer to ensure the total calcination of the precursor.

TEM micrographs of the catalysts were obtained with a Philips CM 200 Supertwin-DX4 high resolution transmission electron microscope. For sample preparation, a suspension of each catalyst was prepared and a drop of these suspensions was dispersed on a Cu grid.

Raman spectra were recorded in a Jobin Yvon Horiba Raman dispersive spectrometer with a variable power He-Ne laser source (632.8 nm) with an input power of 0.9 nm using a 10× objective for every wavelength. The detector is a CDD Peltier-cooled detector.

H_2 temperature-programmed reduction (H_2-TPR) experiments were carried out to 0.080 g of catalyst previously treated with a He flow (35 ml min^{-1}) at 100 °C for 30 min. After cooling to room temperature, the H_2 consumption was studied between this temperature and 800 °C, by using an Ar/H_2 flow (48 ml min^{-1}, 10 vol.% of H_2) and under a heating rate of 10 °C min^{-1}. Water formed in the reduction reaction was removed in an isopropanol-liquid nitrogen trap and a cold finger (−80 °C). The H_2 consumption was measured with an on-line gas chromatograph (Shimadzu GC-14A) provided with a TCD. The H_2 consumed (TPR) was quantified by calibration with pure CuO as reference compound (Aldrich), assuming a total reduction of CuO to Cu^0.

X-ray photoelectron spectra were collected using a Physical Electronics PHI 5700 spectrometer with non-monochromatic Mg Kα radiation (300 W, 15 kV, and 1253.6 eV) with a multi-channel detector. Spectra of pelletized samples were recorded in the constant pass energy mode at 29.35 eV, using a 720 μm diameter analysis area. Charge referencing was measured against adventitious carbon (C 1*s* at 284.8 eV). A PHI ACCESS ESCA-V6.0 F software package was used for acquisition and data analysis. A Shirley-type background was subtracted from the signals. Recorded spectra were always fitted using Gaussian–Lorentzian curves in order to determine the binding energies of the different element core levels more accurately. Short irradiation time spectra of Cu 2*p* and C 1*s* were first registered to avoid as much as possible the photoreduction of Cu^{2+} species.

2.3. Catalytic tests

Catalytic tests were carried out in a fixed bed reactor at atmospheric pressure. The catalysts (0.150 g), with a particle size (0.050–0.110 mm) were introduced into a tubular stainless steel reactor (5 mm i.d.) with a thermocouple inside which is in contact with the catalysts. The samples were pre-treated in-situ under flowing air for 30 min at 400 °C, followed by cooling to room temperature in He flow. The contact time W/F was 0.18 g s cm^{-3} (GHSV = 22000 h^{-1}). In most experiments, the reaction mixture